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Electroplating Plant Operating Conditions Related to Wastewater Sludge Leachability

Centec Corp.
Reston, VA

Prepared for

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Cincinnati, OH

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16. ABSTRACT

The objective of this project was to characterize the operating variables and wastewater sludges from six electroplating plants conducting a wide variety of plating operations so that the information developed would be applicable on an industry-wide basis. The results of the study in which untreated wastewaters were collected from each of six AES member plants, chemically treated to provide solid waste sludges are presented. The solids were separated, and the effluents analyzed for hazardous metals. All of the sludges were subjected to the ASTM "Method A" extraction procedure and hazardous metals analyses were conducted on the leachate. During the study, the EPA Extraction Procedure (EPA-EP) was distributed nationally. As the EPA-EP was one test of the hazardous properties of electroplating sludges under the Resource Conservation and Recovery Act (RCRA), the EPA-EP tests, rather than the ASTM Method A extraction procedure, were replicated for the six plants. All tests, chemical treatment, pH, separation, sludges generation, and extraction procedures were replicated. An in-depth statistical study was also performed of the analytical data for which sufficient information was available.

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Prepared by
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CENTEC Corporation
Reston, Virginia 22090

Under Contract No. WE-2007-8 and
Cooperative Agreement CR808501-01-0, Subcontract CC-371-001

For

American Electroplaters' Society

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SECTION 1

ABSTRACT

In a recent study, "Electroplating Wastewater Sludge Characterization," conducted cooperatively between the American Electroplaters' Society (AES), and the Industrial Environmental Research Laboratory of the U.S. Environmental Protection Agency (U.S. EPA), the leaching characteristics of sludge generated by electroplating wastewater treatment systems were evaluated. One of the recommendations resulting from the study was to further investigate what effect the primary operating variables of the treatment system had on both the effluent quality and the leachability of heavy metals from the sludges. This report presents the results of a study designed to accomplish these goals.

The objective of the project was to characterize the operations and wastewater sludges from six electroplating plants conducting a wide variety of plating operations so that the information developed would be applicable on an industry-wide basis.

The report presents the results of a study in which untreated wastewaters were collected from each of six AES member plants. An orientation sampling, analyses, and wastewater treatment study were conducted for one plant (Plant #7).

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The data from Plant #7, such as selection of treatment chemicals, pH, and several variations of sludge handling lead to various modifications of a test plan and evaluations in wastewater treatment for the other five plants. These changes were confined to the chemical screening and dewatering tests. The wastewater treatment and sludge generation used for Plant #7 were calcium oxide (lime), NaOH (caustic soda), and Na_2CO_3 (soda ash), at pH 7, 8.5 and 10. These data show little difference in sludge characteristics produced at pH 7 and 8.5, and resulted in elimination of tests at pH 7 for the remaining five plants. All sludges were subjected to the ASTM Method A extraction procedure and hazardous metals analyses of the leachate (Section 11). During the study involving Plant #7, the EPA Extraction Procedure (EPA-EP) (Section 11) was distributed nationally. As the EPA-EP was one test of the hazardous properties of electroplating sludges under the Resource Conservation and Recovery Act (RCRA), the EPA-EP tests, rather than the ASTM Method A extraction procedure, were replicated for the subsequent five plants. All tests, chemical treatment, pH, separation, sludge generation, and extraction procedures were replicated. (A schematic of the test program and analytical plan is given in Figure 1-1).

The full projected plan of testing, except for the centrifuge test, was followed for all six plants. The laboratory centrifuge was unable to separate the solids and water satisfactorily for several of the plant- and laboratory-generated samples.

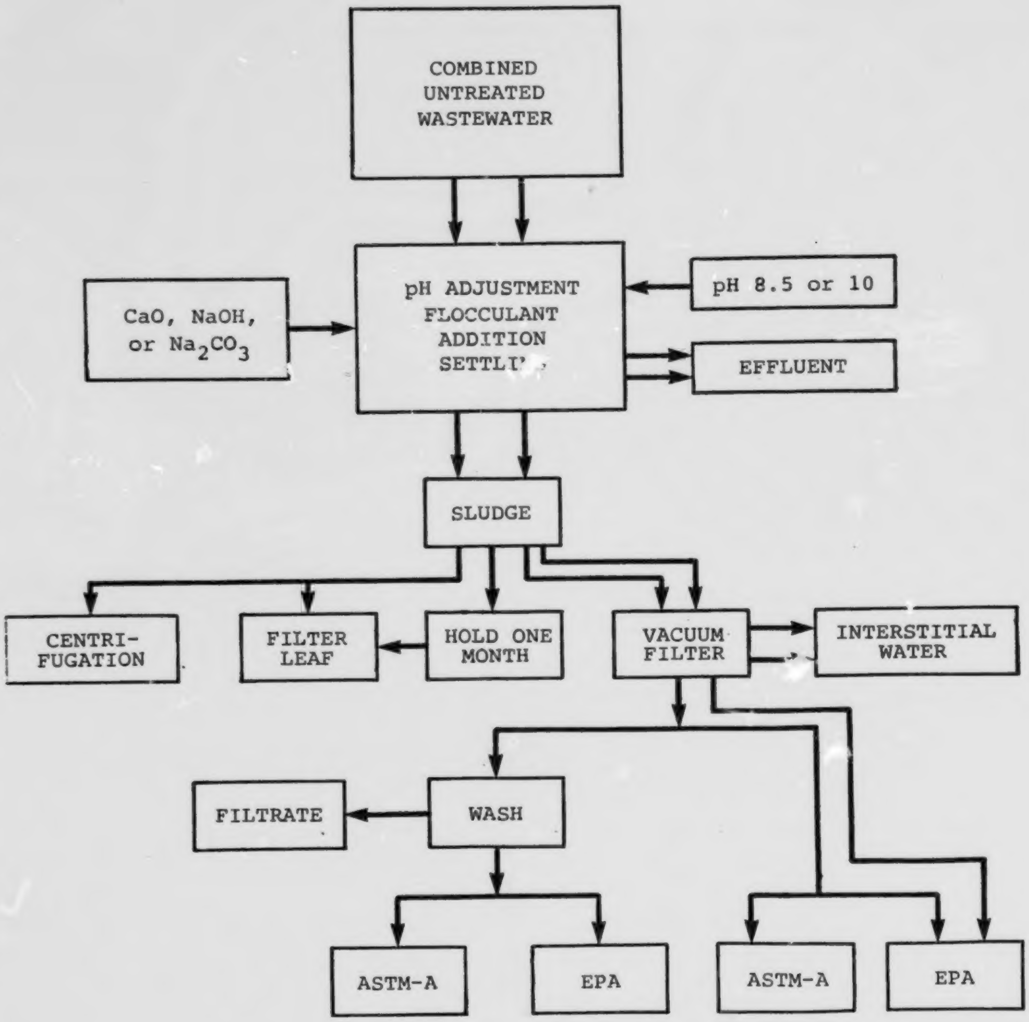
COMBINED UNTREATED WASTEWATER
CaO, NaOH, or Na_2CO_3
pH ADJUSTMENT FLOCCULANT ADDITION SETTLING
pH 8.5 or 10
EFFLUENT
SLUDGE
CENTRI-FUGATION
FILTER LEAF
HOLD ONE MONTH
VACUUM FILTER
INTERSTITIAL WATER
FILTRATE
WASH
ASTM-A
EPA
ASTM-A
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Figure 1-1. Test Program and Analytical Plan

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An in-depth statistical study was performed for analytical data for which sufficient information was available.

SECTION 2

CONCLUSIONS

The conclusions drawn as a result of tests conducted and observations made are relevant only to the plants which were sampled. It is likely that the results will be meaningful to many electroplating shops with similar wastewater characteristics.

Considerable lack of agreement was found between the analytical results for replicate samples prepared by the same technique. This scattering effect gives a surprisingly high background or random variation. This is especially true in samples containing chromium (+6). Against such a background, only rather large changes in sludge leachability could be said to correlate to given treatment parameters with statistical significance. In spite of this masking effect, some correlations appeared to be significant, and the following conclusions can be drawn from the results:

- In the screening tests, the ability of wastewater treatment variables to influence extract quality by variation of treatment parameters was apparently plant specific. The ability to influence extract quality appears to vary among metals under consideration.

- Optimum flocculant and flocculant concentration were determined for each plant's wastewater. A sample jar test was developed to enable plant operators to do their own evaluations.

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- The treatment chemical and pH affected the solids content of the wastewater sludges. The higher solids sludge produced by CaO at pH 10. Less solids were produced by NaOH and Na_2CO_3 and were the same at pH 8.5 and 10.

- The leachability of metals was lower when performed by the ASTM-A extraction procedure than by the EPA-EP extraction. The pH that produced the least leaching was different for each plant. The parameters (pH, treatment chemical, or interaction) that showed a statistical significance for a plant can only be said to be significant for that particular plant. No generalities could be found to apply to sludge leachability.

- The interstitial or free water associated with the sludges had lower metal levels than the effluent waters.

- The precipitation chemical had little effect on sludge dewatering by centrifuge and vacuum filtration. The fresh sludges that dewatered fastest during vacuum filtration all were at pH 8.5. In most cases, fresh sludge dewatered faster than aged sludge though not exclusively. Each plant's sludge behaved differently.

- No quick acceptance test related to the EPA Extraction Procedure was found that could be broadly applied to al plants. Each individual plant may be able to develop a quick acceptance test that applies to its own sludge. However, potential for development of a quick-acceptance test for segregated landfills (ASTM-A) was discovered.

During the sampling portion of the study, it was observed that many waste treatment areas within the electroplating shops were not being operated as well as the equipment would allow. Control instrumentation in some shops was not being properly maintained and therefore could not treat the wastewater properly. In other shops, important indicators were missing so that the effectiveness of treatment was never known.

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SECTION 3

RECOMMENDATIONS

The following recommendations are based on observations made during the testing and engineering evaluations of the data.

- To determine if some of the more positive conclusions are valid, such as the use of CaO or NaOH, selection of pH, the use of selected flocculants, etc., are valid and to what magnitude, it is recommended that these variables be studied at one electroplating plant. The study would involve operating the plant under existing conditions, and then operating for a week at steady state with one or more selected changes. The testing of plant effluents and wastewater sludges would be analyzed and the data evaluated in the same manner as described in the report.

- The data for each plant participating in the study was given to plant management with a request for comments, suggestions and criticism. No replies were received. Perhaps the AES might be of assistance in obtaining feedback even if it is generalizations.

- A study to determine the "in practice" variability of the EPA-EP and the ASTM-A extraction should be undertaken. This request has come from many others using the two procedures, and the data from this report also indicates the need for such a study.

- The testing procedures and their evaluations should be incorporated into a "Standard Electroplaters Wastewater Evaluation Procedures," which can be of general interest and value to individual plant operators who wish to make their own in-plant studies.

- Additional data should be obtained and necessary analysis performed in order to derive a quick acceptance test for operators of segregated nonhazardous waste landfills, based on the significant correlations between filtrate and ASTM-A extract results found in the present study.

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SECTION 4

DESCRIPTION OF PLANT, PLANT PROCESSES, AND SAMPLING

4.1 PLANT SELECTION CRITERIA

An earlier study,[1] from which the current study developed, thoroughly investigated the wastewaters and attendant sludges from 12 electroplating shops. To utilize on the data generated from that study, six of the participating plating shops were selected for this current project. Selection was based on the variety of metals utilized, the wastewater treatment system, and the leaching characteristics of the plants' sludge. The presence of cadmium in the plants' wastewater was highly desirable as cadmium appears to be a problem metal with regard to its leaching characteristics. The facilities designated as Plants 2, 3, 4, 6, 7 and 8 were selected for this study as previous testing showed significant quantities of cadmium, chromium, nickel, zinc, copper, and aluminum present in their wastewater and sludge. Other selection factors included: good cooperation from plant management, and that the plants' sludge had EPA-EP extract levels above the limits that EPA considers hazardous. This last factor was considered as an opportunity to demonstrate the benefits of the current project if indeed the sludges could be rendered nonhazardous by EPA's definition.

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[1] Meredith, J. W., J. A. McCarthy and A. Procko, Electroplating Wastewater Sludge Characterization. EPA-600/52-81-064, U.S. Environmental Protection Agency, Cincinnati, Ohio, May 1981.

4.2 PLANT OPERATIONS

Plant 2 is a captive shop which uses chromate dips and plates acid zinc and acid cadmium onto metal screws. One barrel line is present in the plant and serves both plating tanks. At the time of this study, the plant was operating 18-20 hours/day, Monday through Friday, and 6 hours on Saturday. Water saving techniques such as counterflow rinsing, dragout tanks, and water savers were in use. The plant generated approximately 50 gpm of wastewater requiring treatment.

Plant 3 is a job shop which barrel and rack plates cadmium and copper, as well as using solder and chromate dips. The plant operates 13.5 hours/day, 5 days per week. The plant uses water saving techniques such as countercurrent rinsing, water savers, and turns off rinses when not in use. This plant generates approximately 170 gpm of wastewater.

Plant 4 is a job shop which plates copper, nickel, and chromium onto zinc die-castings. One manual rack line is present in the plant. The plant has 18 rinses which vary from still, overflow, closed-loop, and cascading. Flow restrictors were used on only three rinse tanks. The chrome-bearing wastewaters are routed to an evaporative recovery unit rather than to treatment and disposal. Still, a certain amount of chrome is carried through

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the system and winds up in the plant effluent. Plant 4 generates approximately 60 gpm of wastewater.

Plant 6 is a captive shop which plates nickel and chrome onto steel. One automatic rack line is used for plating, and one manual rack line is used for stripping. The shop uses water saving techniques such as counterflow rinsing, spray rinsing, dragout tanks, and flow restrictors on all running rinses. The plant operates an average of 16 hours/day, 5-1/2 days per week. Approximately 30 gpm of wastewater is generated.

Plant 7 is a job shop which plates brass, bronze, cadmium, chromium, copper, nickel, and zinc. The plant also anodizes and bright dips aluminum. During our visits, the bronze, cadmium, and black chrome plating lines were not in operation. Fourteen plating lines are in use at Plant 7 which is comprised of automatic barrel and rack lines. Plating and anodizing lines operate 16 and 8 hours/day, respectively. This plant generates approximately 120 gpm of wastewater.

Plant 8 is a job shop which plates copper, nickel, and chrome onto plastic. The system is composed of one manual rack plating line. Plating onto plastic requires that Plant 8 use an acid copper bath rather than alkaline copper cyanide. The plant uses 23 rinses that include still, overflow, closed-loop, and cascading rinse tanks. Flow restrictors were used on all but three rinse tanks. This plant generates approximately 50 gpm of wastewater.

Section 7 contains more detailed information concerning the six plating shops and describes the electroplating wastewater treatment plants' operation in greater detail.

4.3 WASTEWATER TREATMENT SYSTEM DESCRIPTION

Refer to Section 7 for the six figures illustrating the wastewater treatment system (WWTS) for the plants used in this study. The flow rates of the incoming streams and treatment retention times are also shown.

The WWTS's in use at each of the plants are typical of systems that segregate their waste streams for separate treatment. Plants 2, 3, 6, 7, and 8 all reduced Cr^{+6} to Cr^{+3}. Section 5.1.4 discusses specific analytical results. These five plants used reducing agents such as sodium bisulfite, ferrous sulfate, or sulfur dioxide in an acidic environment to carry out the chemical reduction. Cyanides were oxidized at Plants 3, 4, and 7 with either sodium hypochlorite or chlorine and caustic in an alkaline environment. The treated chromium and/or cyanide waste streams are then combined with the other acid/alkali wastewater streams where pH adjustment with lime takes place. Generally, all six plants had their pH set-point at 10. Plants 4, 6, 7, and 8 added flocculating agents to the combined wastewaters to improve settling of the metal hydroxides in the clarifier. Overflow from the clarifier was discharged to the plant sewer while underflow went to further thickening and/or dewatering before disposal.

Plants 2 and 3 utilized, to varying degrees, integrated treatment. The chemical treatment of the rinse water was integrated into the operation of the plating line. Integrated treatment involves continuously treating rinse water during, or immediately after, the rinsing process. Plant 2 has a treatment tank and feed sump corresponding to each rinse tank. The rinse water is continuously circulating from the rinse tank to the sump to the treatment tank and back to the rinse tank in a completely closed-loop fashion. Water is added only when required to adjust the tank level. The continuous treatment of the rinse water produces increasing quantities of metal hydroxides that go back to the rinse tank. The metal hydroxides are settled out daily and transferred to another settling tank, and finally filtered. Plant 3 uses integrated treatment for its CdCN rinse water. The cyanide rinse tanks are used as the first stage of cyanide oxidation. A slip-stream of this treated rinse water is combined with all other cyanide rinse water and goes through a second stage of cyanide oxidation, and on to further treatment.

The additional plant information presented in Section 7 describes the plants' WWTS's in greater detail and contains a list of the control parameters available, their set-points, and the observed values.

4.4 SAMPLE SITES AND COLLECTION

During the previous AES study mentioned earlier, detailed plant data were not collected. Therefore, a 1-man presampling survey was required for Plants 2, 3, 4, 6, 7, and 8 to identify: plating operations; type and quantity of rinses; potential sampling sites; number of samples required; and the operating procedures and chemicals necessary for the wastewater treatment system. After completion of a sampling plan for each of the plants, a sampling team of one or two men, depending on the size and complexity of the plant, visited each plant, noted the flow rates of individual streams where necessary, observed operations for anything unusual, and collected the appropriate samples. Wastewater and sludge samples were shipped to CENTEC Analytical Services (CAS) where they were tested according to the analytical plan described in Section 5.

Sample sites are shown in Section 7 along with a table listing the sample points and codes for each plant and how much sample was taken at the various points in the plants.

Liter samples were taken in order to allow for an evaluation of the performance of individual subsystems, such as chrome reduction, and the overall WWTS. As it was impossible to collect an untreated sample of a plant's combined wastewater, the individual wastewater samples were combined in the laboratory in proportion to their relative flow rates in the plant. Drum samples to be used in the experimental program were taken of all wastewater streams at locations upstream of the plant's pH adjustment system. Sludge samples were collected at the point where they would otherwise be transferred to a disposal facility.

The goals of the project did not include an analysis of the effects of chrome reduction or cyanide destruction systems on leaching characteristics and, therefore, the drum samples of these two waste streams were obtained after their individualized treatments. This goal was met for all but Plant 7. In this instance a complication developed with the cyanide stream. As discussed, the presence of cadmium was highly desirable for this study and was an important factor in selecting Plant 7 for investigation. On the day of sampling, the cadmium line was not operating and therefore a bucket of CdCN solution was purposely dumped into the segregated cyanide treatment line. Due to retention times, it was not possible to collect samples of the treated stream; instead, the untreated stream was sampled. It was assumed that the laboratory could perform the cyanide destruction in a manner similar to the plant's system.

For the six plants studied, the underflow from the plants' clarifier was sampled, as this would represent the feed to a mechanical dewatering system if one were present. For this study, it was decided that samples of underflow directly from the clarifier would more closely resemble the more general case of metal finishing treatment sludge than would sludge from a thickener or from a dewatering device. The underflow characteristics would then be used as a basis of comparison for the results of the testing program.

Retention times and flowrates for each treatment step were calculated from data obtained in the plant. If capacities of waste treatment tanks were not readily available, tank measurements were made by the survey team. Flowrates were confirmed by several methods. These include: counting rinse tanks and measuring overflow rates, including some allowance for cooling water, condensate, sanitary water, etc.; reading water meters when available; and measuring the inflow and outflow of wastewater sumps. From flowrates and tank capacities the retention times were calculated.

SECTION 5

TEST PLAN AND RESULTS

5.1 TEST PLANNING AND PREPARATION

5.1.1 TEST PLAN

The purpose of the overall test program was to determine the effect of wastewater treatment chemicals and pH on the leaching characteristics of the sludges generated. The effect of the treatment chemicals on the dewaterability of the sludges by filtering and centrifuging was also to be determined. To accomplish these goals, a detailed test plan was prepared which covered: (1) wastewater preparation; (2) simulation of the plant treatment; (3) screening tests; (4) dewatering tests; (5) analysis of the results. Screening tests were to be performed to determine the precipitation chemical and pH combination which would produce a sludge with the best leaching characteristics without reducing effluent quality. Dewatering of the sludge produced by each treatment chemical followed, utilizing the pH value at which each chemical performed best during the screening tests.

5.1.2 DISCUSSION OF THE EPA EXTRACTION PROCEDURE

The Environmental Protection Agency Extraction Procedure[2] (EPA-EP) Toxicity is one of four criteria for determining whether a solid waste exhibits hazardous characteristics under the Resource Conservation and Recovery Act (RCRA).

The EP Toxicity criterion was established to determine the leachability of an industrial waste under conditions of co-disposal with municipal wastes in a landfill. This criterion is designed to identify wastes which leach hazardous concentrations of toxic constituents into the groundwater under conditions of improper disposal or improper management of disposal sites.

A representative sample[3] (minimum size 100g) of the sludge is separated into its component phases by filtration through a filter having a pore size of 0.45 micrometers. The filtrate is stored at 1 to 5°C (34-41°F). The solid portion is prepared for extraction by reducing the particle size such that it will pass through a standard 9.5 mm (3/8") sieve. The solids are placed in an extraction container with 16 times their weight of deionized water. The mixture is stirred or agitated sufficiently to prevent stratification and to insure that all sample surfaces are continuously brought into contact with the extraction fluid.

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[2] Federal Register, May 19, 1980, pp. 33127-8, Vol. 45, No. 98.

[3] "... representative samples exhibit the average properties of the universe or whole," ibid, Part 260 Definitions, Definition of Representative Sample, p. 33069.

After the solid material and the extraction fluid are placed in the extraction container, the pH of the solution in the container should be measured. If the pH is greater than 5.0 the pH of the solution should be decreased to 5.0 ± 0.2 through addition of 0.5 N acetic acid. If the pH is less than or equal to 5.0 no acetic acid should be added. The pH should be monitored and adjusted until a maximum of 4 ml of 0.5 N acetic acid has been added per gram of solid undergoing extraction. The extraction is carried out between 20 to 40°C (68-104°F) for 24 hours.

Following the extraction, the extract is separated from the solids by filtration through a 0.45 micrometer filter. The extract is diluted to a volume equal to 20 times the weight of the initial solids. The filtrate from the raw sludge is added to the extract and the combined liquid is the EP extract which is analyzed for the following metals:

Metal	Maximum Concentration (mg/l) of Metals for Characteristics of EP Toxicity
As	5.0
Ba	100.0
Cd	1.0
Cr	5.0
Pb	5.0
Hg	0.2
Se	1.0
Ag	5.0

5.1.3 DISCUSSION OF THE ASTM METHOD A EXTRACTION PROCEDURE

The ASTM Method A (ASTM-A) extraction procedure is considerably different from the EPA-EP. This extraction procedure is utilized to evaluate the leaching characteristics of an alkaline metal hydroxide sludge placed in a segregated hydroxide landfill.

Any reasonably sized sample of sludge can be used in the extraction. The sample is weighed without the phases being separated and four times this weight of deionized water is added for the extraction. The container is capped, agitated for 48 hours, allowed to separate, and then decanted. The decant is used for toxic metals analyses. No pH maintenance is attempted.

5.1.4 ANALYTICAL RESULTS FOR PLANT SAMPLES

The analytical results for the plant samples obtained as listed in Table 4-1 are shown in Table 5-1. This analysis was performed in order to characterize the performance of the plant operations during the sampling period. Numerous apparent inconsistencies are present in the table, some due to the time lag associated with the wastewater passing through a particular piece of equipment.

Plant personnel were contacted in an attempt to explain the inconsistencies found in their analytical results. In some instances, plant personnel did not have any answers. The inconsistencies and explanations are as follows: Plant 2 results

Table 5-1

Analytical Test Results for Actual Plant Samples (mg/l)

Plant 2

Sample Description	pH	TDS	TS	Cd	Cr^T	Cr^{+6}	Zn
Yellow Chromate	1.59	28,000	35,100	25.4	19,070	770	3,020
Zinc Bath	5.43	168,200	270,000	0.37	<0.1		22,500
Cadmium Bath	1.98	87,500	99,500	14,600	8.49		1,850
Acid Bath	0.74	7,760	12,500	372	1.57		645
Effluent	11.15	16,100	16,100	3.68 0.37*	6.08 0.20*	0.08	7.73 0.66*
Spent Acid	1.72	2,530	4,920	38.6	66.8	<0.05	499
Blue Chromate	0.62	27,300	31,300	0.94	343	74	2,580

---

*Dissolved metal.

**Metal concentrations are those found in the EPA-EP extract.

Table 5-1

Analytical Test Results for Actual Plant Samples (mg/l) (Continued)

Plant 3

Sample Description	pH	TDS	TS	Cd	T Cr	+6 Cr	Zn	CN	Cu
Clear Chromate	7.18			3,980	2.02	<0.05			
Yellow Chromate	12.38			0.91	705	685			
CdCN Rinse	12.76			-				298.7	
Other CN Rinse	10.81			60.5				42.2	2.70
Acid Rinse	11.97			54.5					11.4
After CN Oxidation	11.22			-				31	
After pH Adjustment	10.90	4,430	5,640	69.5	45.8				2.18
Effluent	11.75			2.90	14.9		0.82		
				1.68*	10.5*		0.51*		1.58*
Centrate	10.43			10.4*	14.6*		4.42*		
Clarifier Underflow**	10.36	5,940	10,700	538	3.55	1.52			
Acid Sump (Barrel)	10.86				1.46				5.17
Acid Sump (Rack)	4.32			106	252				0.76
After CN Oxidation	10.76			2.46					0.09

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*Dissolved metal.

**Metal concentrations are those found in the EPA-EP extract.

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Table 5-1

Analytical Test Results for Actual Plant Samples (mg/l) (Continued)

Plant 4

Sample Description	pH	TDS	TS	Cu	Ni	Cr^T	CN(diss)	Zn
Treated Cyanide	10.07						5.75	
After pH Adjustment	12.07			42.3	31.1	1.33		
Effluent	11.70			1.15	2.65	1.51		
				0.11*	0.96*	0.92*		
Filtrate	11.88			1.41*	2.43*	1.30*		
Treated Cyanide	10.01			80.6	15.8	0.62		0.36
Ni Rinse	7.32			6.57	165	2.09		2.59
Cleaner Rinse	9.13			0.75	0.33	0.34		9.00
Sludge**	10.66	8,200	138,000	34.9	55.3	158	<0.02	25.0

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*Dissolved metal.

**Metal concentrations are those found in the EPA-EP extract.

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Table 5-1

Analytical Test Results for Actual Plant Samples (mg/l) (Continued)

Plant 6

Sample Description	pH	TDS	TS	Ni	Cr^T	Cr^{+6}
After Mix Tank	11.56	2,000	5,250	<0.1	<0.5*	<0.05
Clarifier Overflow	11.80			<0.1	<0.5*	<0.05
Effluent	9.79			<0.1 <0.1*	<0.5 <0.5*	<0.05 <0.05*
After CR Reduction	1.93			2.59	352	<0.05
Combined Acid Rinses	2.63			18.5	45.6	<0.05
After Mix Tank	12.36			0.35	1.11	<0.05
Sludge from Clarifier**	11.78	1,940	81,100	18.5	45.6	<0.05

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*Dissolved metal.

**Metal concentrations are those found in the EPA-EP extract.

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Table 5-1

Analytical Test Results for Actual Plant Samples (mg/l) (Continued)

Plant 7

Sample Description	pH	TS	TDS	Cd	Cr^T	Cr^{+6}	Cu	Mn	Ni	Zn	Al	CN^T
Acid/Alkali	6.71	1,080		0.10	0.67	<0.05	1.35	0.30	43.0	13.0	0.62	
Acid/Alkali	6.88	994		0.06	0.49	<0.05	1.31	0.26	55.5	12.5	0.58	
Untreated Cr	2.23	810		<0.01	50.0	6.60	0.12			180.0		
Treated Cr[1]	1.55	1,850		<0.01	44.5	<0.5	0.11	0.14	<0.10	143	0.75	
Untreated CN	7.69	7,510		25.2	<0.1		10.2	0.10		265		21.5
Untreated CN	12.13	3,040		20.2	0.05	<0.05	8.12	0.18	<0.10	137	0.50	440
Treated CN	3.26	7,880		13.5	0.08		6.0	0.15		215		4.40
Untreated Al	2.41	1,520		0.04	0.52	<0.05	0.80	0.25	0.98	4.48	78.0	
Combined Streams	8.5	2,360	1918	0.08	3.05		0.85	0.13	10.0	27.3	20.6	
Clarifier Effluent	10.1	2,280	2226	<0.01	0.25		0.10	<0.05	3.6	2.88	9.9	
Clarifier** Underflow	8.53	7,850	2150	0.14	4.72	<0.05	2.98	0.90	165	762	0.75	
Sludge Bed**				4.75	0.50	<0.05	1.32	2.62	46	516	1.12	

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[1] This sample was split and sent to an independent laboratory. Comparison of analytical results is shown on the next page.

*Dissolved metal.

**Metal concentrations are those found in the EPA-EP extract.

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Table 5-1

Analytical Test Results for Actual Plant Samples (mg/l) (Continued)

Plant 8

Sample Description	pH	TDS	TS	Cu	Ni	Cr^T	Cr^{+6}
After pH Adjust	9.64	2,500	4,100	43.5	37.7	298	
Clarifier Overflow to Effluent	9.16			1.09 1.15*	0.38 0.55*	0.22 0.10*	
Filter Filtrate to Effluent	9.45			0.50	0.73	0.77	
Chromium Waste	2.14	1,600	1,790	48.5	55.0	2,500	<0.05
Acid/Alkali Rinses	3.22	980	1,100	50.4	43.0	3.68	
Clarifier Sludge**	9.84	2,400	11,900	16.1	44.1	111	0.08

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*Dissolved metal.

**Metal concentrations are those found in the EPA-EP extract.

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Table 5-1

Analytical Test Results for Actual Plant Samples (mg/l) (Continued)

ERC/LANCY

ANALYSIS REPORT FORM

CLIENT CENTEC
P.O. # 5010-41 FAS
NOTEBOOK CODE

DATE OF SAMPLING 12/11/80
DATE RECEIVED
DATE OF REPORT 1/9/81
REPORT ANALYSIS TO F. Steward

SAMPLE HISTORY Chromium VI Treatment System (Drum 3)

	CENTEC Analysis (mg/L)	Lancy Analysis (mg/L)
pH	1.55	1.65
Cr^{6+}	-	<0.01
Cr^{T}	44.5	51
Cu	0.11	0.12
Mn	0.14	0.14
Ni	<0.10	0.08
Zn	143.0	240
Al	0.75	1.0
Cd	-	0.03

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show high zinc levels in the chromate and cadmium baths. During our sampling, the zinc treatment system was not performing as it should have due to a broken pH controller. This resulted in inadequate treatment and carry-through. There was also an extremely low level of chrome in the blue chromate bath which Plant 2 personnel have not been able to explain. The chromate dips at Plant 3 had a very high concentration of cadmium which was the result of the chromate dip stripping small amounts of cadmium from each part. Yellow chromate was not being treated as a result of a broken pH meter. The spent chromate bath was not being made acidic so reduction of Cr^{+6} to Cr^{+3} could not be performed. The acid rinse water at Plant 3, labeled L5, had a pH in the alkaline range. This stream included rinse water from alkaline cleaners. Personnel at Plant 4 could not answer our questions regarding the fact that all metals were found in each of the segregated rinse water streams. This same problem appeared in the results from Plant 8. Project personnel theorize that during the plating operations each metal is deposited into crevices in the racks and later the metals are removed in the acid plating solutions of other tanks. The untreated chrome stream for Plant 7 shows 50 mg/l of chrome while the treated chrome stream shows only 44.5 mg/l. As can be seen in Figure 4-5, there is a 101 minute retention time in the chrome reduction system which, along with the mixing that occurs, can easily account for the apparent inconsistency noted.

Underflow from the plants' clarifiers was subjected to the EPA extraction procedure which is the primary EPA test for determination of whether or not the material should be considered a hazardous waste.

The clarifier underflow would not be classified as hazardous for Plant 7, but Plants 3, 4, 6 and 8 would be classified as hazardous because of high cadmium or chromium in the EP extract. The hazardous level for cadmium is 1.0 mg/l and for chromium is 5.0 mg/l. Of the five metals of concern to this study (cadmium, chromium, copper, nickel, and zinc), only cadmium and chromium are considered hazardous and must be measured in the EPA-EP extract of the clarifier underflow. The ASTM-Method A extraction procedure was also used to test the underflow. The underflow test results were used as the standards of comparison for sludges generated by this test program because the underflow represents the more typical disposal problem which would be experienced by plating shops.

5.1.5 WASTEWATER PREPARATION AND FLOCCULANT SELECTION

Because of the way the plants were operated, it was impossible to collect an untreated sample of combined wastewater. Therefore, 200 liters (53 gallons) of each segregated stream were collected as described previously.

Prior to combining the segregated streams, it was necessary to check for the presence of excess cyanide in the cyanide wastewater stream of Plants 3, 4 and 7. The laboratory used calcium hypochlorite ($Ca(OCl)_2$) to oxidize the cyanide if necessary. An entire drum of cyanide wastewater was treated in a single batch. This was done by first adjusting the pH of the cyanide wastewater to between 8.5 and 9.0 with caustic and then adding $Ca(OCl)_2$ to maintain a 20 mg/l excess Cl_2 level. Good agitation was supplied for at least 60 minutes. During the 60 minute agitation period, a spot test with starch iodide paper was used. The paper turns blue as long as there is at least 20 ppm of Cl_2 present. After the 60 minute agitation period, the contents of the drum were analyzed for cyanide. Cyanide must be below 1 ppm before further testing can proceed.

The individual wastewater streams were then combined in the laboratory in proportion to their flow rates in the plant, as shown in Table 5-2. This resulted in an untreated mixture with the composition shown in Table 5-3.

The mixtures in Table 5-3 have no analogous counterparts in the samples collected at the plants because by the time the streams are combined at the plant, they have been pH adjusted.

Studies were conducted on portions of the simulated wastestream of each plant to determine an optimum polymer flocculating agent and its effective concentration. In this study, four anionic polymer flocculating agents were evaluated against the flocculating agent employed at the plant to determine which produced the best settling rates and flocculant characteristics. The results of this study were qualitative and are shown in Table 5-4.

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Table 5-2

Wastewater Stream Relative Contribution

	Relative Portions					
Waste Stream	Plant 2	Plant 3	Plant 4	Plant 6	Plant 7	Plant 8
Acid/Alkali	8.47 parts	14/1.0 part*	4.15/1.0 parts	2.0/3.33 parts*	4.33 parts	7.4 parts
Chromium	1.0 part			1.0 part	1.33 parts	1.0 part
Cyanide		1.55 parts	3.48 parts		1.0 part	
Aluminum					1.0 part	

---

*Plants 3, 4 and 6 had two distinct acid/alkali lines going to the pH adjustment tank.

Table 5-3

Composition of Combined Untreated Wastewater

	Concentration of Metals for Each Plant (mg/l)					
Metal	Plant 2	Plant 3	Plant 4	Plant 6	Plant 7	Plant 8
Cadmium	44.7	16.4			0.36	
Chromium	21.0	16.4	1.29	22.0	10.0	303
Copper		4.45	35.5		0.59	50.2
Nickel			85.6	8.88	23.0	44.4
Zinc	82.9		2.47		55.0	

Table 5-4

Flocculant Results

Optimum Flocculant Determined in Laboratory	Concentration of Flocculating Agent (mg/l) Plant 2	Plant 3	Plant 4	Plant 6	Plant 7	Plant 8
1. American Cyanamid, Maginfloc 836-A	2.0					
2. Calgon, WT-3000		0.5				
3. Separan AP-273™			1.0			
4. Allied Colloids, Percol™				2.0		
5. Separan AP-273™					1.32	
6. Separan AP-273™						2.0
Plant-Supplied Flocculants						
1.	N/A					
2.		N/A				
3. Separade P-3						
4. Allied Colloids, Percol™				6.0 (approx.)		
5. Hercules Chemical, Hercufloc™					26.42	
6. EPEC, Flocculant 306						4.5 (approx.)

N/A = Not applicable

Settling tests indicated that the flocculants used at the plant were not very effective in speeding up the settling process of the precipitated particles. Jar tests utilizing five flocculants in addition to the plant flocculant were performed to find one which speeded the settling rate adequately for testing purposes. Each test batch (jar test) was agitated for 10 minutes after pH adjustment (prior to the addition of flocculant). A brief agitation period followed the flocculant addition after which the settling time and volume of solids settled were noted. The flocculant which produced the largest flocs and had the most rapid settling time was then used for all sample preparations for that plant, except for the simulation of the plant sludge, discussed below, which used the plant-supplied flocculant. In Table 5-4, the optimum flocculant for each plant is shown by a star next to the concentration of that flocculant. Concentration of flocculant used in the plant are in parentheses.

Settling tests were performed by evaluating each flocculating agent over a concentration range of 0 (blank) to 8 mg/l. Plant 2 used no polymer flocculating agent. Magnifloc 836A and Calgon WT-3000 performed well on its simulated wastestream. Magnifloc 836A was effective at a much lower concentration and was chosen for future studies. Plant 3 also used no polymer to aid settling in their treatment. Very slow settling rates were observed without added flocculating agents. Only Calgon WT-3000 resulted in improved settling and floc characteristics. It was effective at a final concentration of 0.5 mg/l. Plant 4 settled well using Separade P-3 (its own choice of polymer), Separan AP273 and Calgon WT-3000. Separan AP-273 was chosen since it was effective at the lowest concentration. Plant 6 used 6 mg/l Percol in its treatment. Percol was found to be effective at 2 mg/l. This was the only plant in which its flocculating agent outperformed the others investigated. Settling tests for Plant 7 indicated that the flocculant used at the plant was not very effective in speeding up the settling process of the precipitated particles. In fact, there was no noticeable difference between settling rates of samples with and without the plant-supplied flocculant. The optimum flocculant was Separan AP-273 at a loading of 1.32 mg/l of wastewater. Plant 8 used EPEC Floc #306 which performed well at 5 mg/l, however, Separan AP-273 and Calgon WT-3000 were equally effective at lower concentrations. Separan AP-273 was effective at 2 mg/l and was used throughout further studies.

5.1.6 SIMULATION OF THE PLANT TREATMENT SYSTEM

To lend credibility to the results of the test program, it was first necessary to duplicate the plants' treatment system in the laboratory. If laboratory generated sludge could closely match the plants' sludge then it followed that modifications to the laboratory procedure might be expected to have similar results at the plants. The acid/alkali, chromium, and cyanide waste streams (as appropriate for each plant) were mixed and pH adjusted with the plant's reagent to the pH set point found in the plant. This mixture was agitated to simulate residence time in the plant pH adjust tank. Settling rates on a 100 ml sample in a graduated cylinder with freshly prepared flocculant as used at the plant and at the plant dosage, were noted. These notations included the logging of settling time and volume of solids settled. The treated mixture was then allowed to settle for the same time as in the plant clarifier, followed by phase-separation by siphoning. The overflow portion was tested for the predominant metals found in the plant, and the underflow, or sludge, was subjected to an ASTM-A extraction (see Sections 5.1.3 and 5.1.2 for details of the ASTM and EPA extraction procedures). The results of this testing were then compared to the actual plant sample results of clarifier overflow and underflow.

With the laboratory set-up, it was necessary to draw off the clear layer from the settling container using a syphon tube. Wastewater was drawn off in this manner until the sludge became visibly disturbed by the process. This approach generated a sludge with more free water than the actual plant clarifier underflow. A correction factor for the ASTM-A test results, therefore, had to be applied to account for the dilution present in the laboratory simulated sludge. This factor was derived from a combination of the different percentages of free water in the two sludges and the dilution water used in the extraction tests. The characteristics of the plant effluent and underflow and the laboratory simulated effluent and simulated underflow are presented in Table 5-5. Some differences in the characteristics were expected due to the variables involved in sampling such as production changes and lag times. Exactly when a difference becomes unreasonable is difficult to specify. Substantial differences occurred with Plants 3, 4, 7, and 8. Copper and nickel were higher in the simulated underflow by a factor of 10 in the Plant 3 results. In Plant 4's results, copper and nickel were higher in the simulated underflow by a factor of 100 and 10, respectively. Nickel was again higher by a factor 10 for Plant 7. For Plant 8, Nickel was lower by a factor of 10. We cannot explain why copper and nickel were consistently higher or lower during the simulation by such a large factor.

One problem arose during the simulation of the plant treatment system. As mentioned earlier, Plant 2 uses completely integrated treatment. Therefore, it was impossible to obtain a sample of untreated wastewater. Instead, samples of acid and plating bath solutions were obtained. The plant rinsewater was to be simulated so that it would represent a more conventional plating operation. From the experience of the project personnel, it was decided to dilute the plating bath and acid bath solutions 100 to 1 in order to represent conventional rinsing. The simulated rinse waters were then combined and treated as described above. Therefore, results of the plant simulation tests for Plant 2 are not applicable and have not been presented in Table 5-5.

Table 5-5

Results of Plant Simulation Tests

(mg/l)

Plant 3	pH	TS	DS	Cd	Cr^T	Cr^{+6}	Cu	Ni	Zn
Plant Underflow (ASTM-A)	10.36	10,700	5,940	0.04	0.95	1.39	0.17	<0.1	
Plant Simulation Underflow (ASTM-A)	10.9	11,000	4,450	0.33	0.11	0.80	1.00	<0.1	
Plant Simulation Underflow with Correction for Dilution				0.55	0.18	1.34	1.67	*	
Plant Effluent***	11.75			1.68	10.5		1.58	<0.2	0.51
Plant Simulated Effluent***	10.9			0.03	17.9		4.73	<0.1	0.05

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*Correction factor cannot be applied.

**After settling for 2.25 hours.

***Analysis was for dissolved metal rather than total metal in order to determine the effectiveness of treatment.

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Table 5-5

Results of Plant Simulation Tests (Continued)

Plant 4

					(mg/l)				
	pH	TS	DS	CN	Cr^T	Cr^{+6}	Cu	Ni	Zn
Plant Underflow (ASTM-A)	10.66	138,000	8,200	<0.02	0.41	0.49	0.06	0.38	<0.1
Plant Simulation Underflow (ASTM-A)	10.5	58,100	--	--	<0.1	<0.05	2.05	1.96	0.02
Plant Simulation Underflow with Correction for Dilution					*	*	6.86	6.56	0.07
Plant Effluent***	11.7				0.92	1.10	0.11	0.96	
Plant Simulated Effluent***	10.5				0.23	0.09	0.80	10.0	

---

*Correction factor cannot be applied.

**After settling for 2.25 hours.

***Analysis was for dissolved metal rather than total metal in order to determine the effectiveness of treatment.

Table 5-5

Results of Plant Simulation Tests (Continued)

Plant 6			(mg/l)			
	pH	TS	DS	Cr^T	Cr^{+6}	Ni
Plant Underflow (ASTM-A)	11.78	81,100	1,940	1.12	<0.05	<0.10
Plant Simulation Underflow (ASTM-A)	11.70	29,800	3,840	0.19	<0.05	<0.25
Plant Simulation Underflow with Correction for Dilution				0.39	*	*
Plant Effluent***	11.80			<0.50	<0.05	<0.10
Plant Simulated Effluent***	11.70			<0.10	<0.05	<0.25

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*Correction factor cannot be applied.

**After settling for 2.25 hours.

***Analysis was for dissolved metal rather than total metal in order to determine the effectiveness of treatment.

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Table 5-5

Results of Plant Simulation Tests (Continued)

Plant 7 (mg/l)

	Cd	Cr^T	Cu	Ni	Zn	TS	DS
Plant Underflow (ASTM-A)	.02	<.05	.04	.38	.65	7,774	2,074
Plant Simulation Underflow (ASTM-A)	<.02	<.10	.06	1.42	0.14	4,375	2,080**
Plant Simulation Underflow with Correction for Dilution	*	*	0.16	3.77	0.37		
Plant Effluent	<.01	.25	.10	3.6	2.88		
Plant Simulation Effluent	<.01	.20	.04	6.90	1.01		

---

*Correction factor cannot be applied.

**After settling for 2.25 hours.

***Analysis was for dissolved metal rather than total metal in order to determine the effectiveness of treatment.

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Table 5

Results of simulation tests
(Continued)

Plant 8				(mg/l)			
	pH	TS	DS	Cr^T	Cr^{+6}	Cu	Ni
Plant Underflow (ASTM-A)	9.84	11,900	2,400	<0.1	<0.05	0.08	0.20
Plant Simulation Underflow (ASTM-A)	9.50	11,500	3,370	<0.1	<0.05	<0.05	0.10
Plant Simulation Underflow with Correction for Dilution				*	*	*	0.03
Plant Effluent***	9.16			0.22		1.09	0.38
Plant Simulated Effluent***	9.5			0.88		0.79	0.55

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*Correction factor cannot be applied.

**After settling for 2.25 hours.

***Analysis was for dissolved metal rather than total metal in order to determine the effectiveness of treatment.

5.2 SCREENING TESTS

5.2.1 TEST PLAN

Screening tests were conducted in order to determine the relationship between treatment chemical and pH on the treatment system effluent and on the extract from the sludges produced. The method utilized to achieve these goals was to take actual untreated electroplating wastewaters and treat them with three common precipitation chemicals: sodium hydroxide (NaOH), soda ash (Na_2CO_3), and lime (CaO). Tests were conducted with each of these chemicals on the combined untreated plant wastewater as described earlier with pH's adjusted to 8.5 and 10 (7, 8.5, and 10 for Plant 7). The wastewater was treated in a manner similar to the plants' treatment system except for the change in chemicals and pH (and the flocculant change noted above) so that the plants could easily implement any recommended changes. Individual waste streams were mixed in the proper proportions, and kept agitated while pH adjusted. Appropriate retention times were used, and after flocculation the mixture was allowed to settle. The water layer (overflow) was decanted and analyzed for its metal content and the sludge layer (underflow) was vacuum filtered. An analysis of the filtrate for metals was performed for comparison to the plant effluent. The sludge cake was then subjected to the ASTM-A and EPA extraction procedures, the extract of which was also analyzed for metals.

To study the leaching characteristics of the screening test sludges, a portion of each sludge after filtering was washed in a filter funnel with 200 ml of deionized water and again vacuum filtered and the sludge subjected to the ASTM-A and EPA extraction procedures. The washing water also was analyzed for metals.

Analytical results from these laboratory tests were compared to each other and to the plant's samples in an attempt to determine which combination of chemicals and pH was performing best with reference to effluent quality and sludge leaching characteristics.

These screening tests were designed in such a way that the extent to which the observed variation exceeds the variation expected due to simple random behavior could be determined. That is, if experimental results seem to indicate that pH or the precipitation chemical does have an effect on the effluent extract quality for one or more metals, it was desired that it be possible to determine with a stated level of confidence that the observed effect is not due to random variation alone.

For that reason, data collection during the sludge characterization experiments was designed to comprise a 2x3-factorial experiment with complete replication. Plant 7 was designed as a 2-factor, 3-level experiment with partial replication. Such an experimental design was chosen to make it possible to perform an analysis of variance in order to determine which of the observed trends are statistically significant.

5.2.2 RESULTS

Tables 5-6 through 5-13 present the results of the screening tests. In the case of Plant 7 where partial replication was performed, only those test points which fall along the diagonal have been replicated.

With reference to Tables 5-2 and 5-3 which show the metal concentrations in the untreated wastewater and plant effluent, respectively, for Plant 2 at pH 10.0 more than 98 percent of the cadmium has been removed by treatment. Chromium and zinc were removed from the effluent with a 99 percent efficiency. At this pH, CaO showed the lowest metal levels in the effluent, although the difference is slight. From Tables 5-8 and 5-9 it is evident that although the metals did not resolubilize and leach out during the ASTM-A procedure, the lower pH of the EPA-EP caused Plant 2 to fail the EPA-EP based on cadmium levels. Results of the EPA-EP at pH 8.5 showed lower metal levels, but still not enough to pass the test. The chromium extract also failed the first time but passed during the replication phase. Chromium levels in the effluent and EPA-EP extract were not affected very much by pH or chemical, except when Na_2CO_3 was used. With Na_2CO_3, chromium was an order of magnitude higher in the EPA-EP extract.

A similar analysis for Plant 3 shows cadmium and chromium removal efficiencies of 91 and 68 percent, respectively, at pH 8.5. At pH 10, cadmium and chromium removal efficiencies were

Table 5-6
Results of Screening Tests for Effluent Samples (mg/1)

Plant 2

	Total Chrome			Hex. Chrome			Cadmium			Zinc		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	0.10	<0.10	<0.10	<0.05	-	-	9.20	10.8	1.17	1.52	1.29	0.80
	<0.10	<0.10	<0.10	<0.05	<0.05	<0.05	6.20	3.95	0.88	0.19	0.60	0.33
pH 10	<0.10	0.11	0.40	-	<0.05	<0.05	0.30	0.38	1.32	0.53	0.60	1.66
	<0.10	<0.10	0.85	<0.05	<0.05	<0.05	0.14	0.28	1.92	0.26	0.34	3.00

Plant 3

	Total Chrome			Hex. Chrome			Cadmium		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	6.22	6.34	6.72	5.03	4.31	5.3	1.05	3.51	1.66
	3.79	3.85	4.55	2.79	2.90	3.14	0.54	0.73	0.94
pH 10	8.72	10.1	8.63	8.35	12.5	6.7	0.39	1.50	3.04
	4.40	5.62	6.02	3.05	3.65	4.25	0.34	0.61	1.44

Plant 4

	Total Chrome			Hex. Chrome			Copper			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	0.19	0.08	0.42	0.15	0.09	0.09	6.80	4.64	10.2	26.4	43.2	33.2
	0.21	0.21	0.27	-	-	-	8.28	7.56	7.50	29.8	40.7	40.0
pH 10	0.37	0.08	0.37	0.11	0.15	0.12	1.22	3.83	9.38	9.68	13.1	15.4
	0.21	0.21	0.21	-	-	-	5.95	3.42	10.7	13.9	10.7	13.4

Note: (-) indicates that Cr^{+6} was not determined because Cr^T was below the detectable limit.

Table 5-6
Results of Screening Tests for Effluent Samples (mg/1) (Continued)

Plant 6

	Total Chrome			Hex. Chrome			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	0.15 0.15	0.05 0.08	0.18 0.28	<0.05 <0.05	<0.05 <0.05	<0.05 <0.05	0.27 0.27	0.24 0.22	0.33 0.27
pH 10	0.05 0.12	0.08 0.21	5.20 1.12	<0.05 <0.05	<0.05 <0.05	<0.05 <0.05	<0.10 0.11	<0.10 <0.10	1.02 0.33

Plant 7

	Chromium			Cadmium			Copper			Nickel			Zinc		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 7	0.12	.10	.09 .06	.25	.48	.30 .34	.03	.04	.03 .04	8.1	8.1	8.9 7.35	2.35	3.5	2.1 1.55
pH 8.5	.17	.23 .16	.17	0.02	.01 .01	.01	.05	.03 .03	.02	2.68	1.5 1.85	2.42	1.00	1.1 .94	.90
pH 10	.23 .16	.22	.34	0.02 <0.01	<.01	.02	.06 .05	.06	.06	0.92 .75	1.08	1.40	1.50 0.82	1.1	1.90

Plant 8

	Total Chrome			Hex. Chrome			Copper			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	1.02 0.58	1.29 10.0	48.3 12.1	<0.1	<0.05	<0.05	1.14 0.76	1.24 1.40	3.01 1.03	0.54 0.55	0.38 1.34	5.91 1.35
pH 10	1.54 1.27	1.93 1.75	180 350	<0.05	<0.05	<0.05	0.94 1.31	1.18 1.28	46.7 42.3	0.73 0.50	0.73 0.66	48.1 36.5

Table 5-7
Results of Screening Tests for Filtrate of the Underflow Samples (mg/1)

Plant 2

	Total Chrome			Hex. Chrome			Cadmium			Zinc		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	<0.10 <0.10	<0.10 <0.10	<0.10 <0.10	- -	- -	- -	9.00 9.00	18.8 13.0	0.54 0.18	0.99 0.43	3.30 0.72	0.31 0.16
pH 10	<0.10 <0.10	<0.10 0.10	<0.10 0.15	- -	- 0.13	- 0.12	0.32 0.17	0.11 0.25	0.18 0.43	0.22 <0.05	<0.05 <0.05	0.19 0.17

Plant 3

	Total Chrome			Hex. Chrome			Cadmium		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	6.18 9.02	7.32 9.48	6.47 8.76	<0.50 1.00	11.5 2.80	6.89 4.33	0.05 0.39	0.46 0.28	0.41 0.37
pH 10	9.76 10.1	11.4 12.5	8.20 13.6	7.73 2.52	13.7 3.81	7.38 3.15	0.08 0.09	0.06 0.07	0.13 0.09

Plant 4

	Total Chrome			Hex. Chrome			Copper			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	0.23 0.25	0.22 0.16	0.50 0.24	0.11 -	0.06 -	0.16 -	5.76 7.47	3.70 7.29	7.88 7.65	23.9 32.6	37.3 47.4	27.9 28.1
pH 10	0.08 <0.25	0.27 0.25	0.40 0.41	<0.05 -	<0.05 -	<0.1 -	3.04 4.32	11.0 7.65	14.1 11.3	12.1 41.2	15.3 12.3	13.8 11.2

Note: (-) indicates that Cr^{+6} was not determined because Cr^T was below the detectable limit.

Table 5-7
Results of Screening Tests for Filtrate of the Underflow Samples (mg/l)
(Continued)

Plant 6

	Total Chrome			Hex. Chrome			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	0.10	<0.05	<0.05	<0.05	-	-	0.27	<0.10	<0.10
	<0.05	<0.05	<0.05	-	-	-	<0.10	<0.10	<0.10
pH 10	<0.05	0.05	0.08	-	<0.05	0.12	<0.10	<0.10	0.11
	<0.05	0.17	0.05	-	0.13	<0.05	<0.10	<0.10	<0.10

Plant 8

	Total Chrome			Hex. Chrome			Copper			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	<0.05	0.07	0.80	<0.05	<0.05	<0.05	0.73	0.97	0.97	0.50	0.50	0.66
	<0.5	0.18	0.39	-	-	-	0.34	1.03	0.80	0.65	0.59	0.84
pH 10	<0.05	0.28	7.60	<0.05	<0.05	<0.05	0.32	0.48	1.30	0.50	0.45	0.45
	<0.5	<0.5	9.15	-	-	-	0.34	0.84	1.40	0.49	0.46	0.52

Note: (-) indicates that Cr^{+6} was not determined because Cr^T was below the detectable limit.

Table 5-8
Results of Screening Tests for EPA-EP Extract of the Underflow Samples (mg/1)

Plant 2

	Total Chrome			Hex. Chrome			Cadmium			Zinc		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	24.0 0.80	21.0 0.35	195.0 1.50	<0.05 <0.13	<0.05 <0.05	<0.05 <0.13	324 480	378 401	378 300	516 601	636 480	672 505
pH 10	48.0 0.90	60.0 0.95	293 4.25	<0.05 <0.13	<0.05 <0.13	<0.05 <0.05	540 465	408 425	516 230	672 555	474 385	588 610

Plant 3

	Total Chrome			Hex. Chrome			Cadmium		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	1.87 1.90	1.95 1.05	1.66 1.31	0.82 0.40	0.11 0.14	0.38 0.12	221 160	268 172	216 176
pH 10	2.71 2.22	2.75 1.58	2.33 1.52	1.01 2.51	0.09 0.53	0.70 0.34	155 140	259 262	310 383

Plant 4

	Total Chrome			Hex. Chrome			Copper			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	0.33 0.74	0.70 1.72	1.02 1.88	<0.25 -	<0.1 -	<0.25 -	739 788	581 697	1110 629	1250 822	937 975	1240 920
pH 10	0.13 <0.25	0.20 1.95	0.16 <0.25	<0.05 -	<0.05 -	<0.25 -	51.5 27	479 562	68.5 335	247 247	1320 1140	1060 975

Note: (-) indicates that Cr^{+6} was not determined because Cr^{T} was below the detectable limit.

Table 5-8
Results of Screening Tests for EPA-EP Extract of the Underflow Samples (mg/1)
(Continued)

Plant 6

	Total Chrome			Hex. Chrome			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	4.75 5.50	1.12 1.25	3.50 5.50	<0.13 <0.13	<0.13 <0.13	<0.13 <0.13	50.0 47.5	32.5 31.2	40.0 48.8
pH 10	0.13 1.25	<0.50 <0.20	0.75 <0.13	<0.13 <0.13	<0.13 <0.13	<0.13 <0.13	10.1 20.5	33.8 37.5	45.0 15.0

Plant 8

	Total Chrome			Hex. Chrome			Copper			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	667 117	131 68.9	41.2 32.1	<0.05 -	<0.25 -	<0.1 -	4.65 4.22	3.05 0.86	7.81 6.12	89.2 59.4	26.7 18.2	182 201
pH 10	683 300	110 120	41.3 49.2	<0.05 -	<0.05 -	<0.25 -	38.9 21.4	7.57 1.72	5.64 16.9	136 59.4	44.2 25.2	161 94.6

Note: (-) indicates that Cr^{+6} was not determined because Cr^{T} was below the detectable limit.

Table 5-9
Results of Screening Tests for ASTM-A on the Underflow Samples (mg/1)

Plant 2

	Total Chrome			Hex. Chrome			Cadmium			Zinc		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	<0.10	<0.10	<0.10	-	-	-	3.55	29.8	0.19	0.16	3.20	0.23
PH 10	<0.10	<0.10	0.19	-	-	0.15	0.02	0.07	0.25	<0.05	<0.05	0.11

Plant 3

	Total Chrome			Hex. Chrome			Cadmium		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	7.19	7.06	5.55	7.44	8.74	8.21	0.09	0.07	0.21
pH 10	7.19	8.49	8.14	8.08	7.44	12.1	0.05	0.05	0.49

Plant 4

	Total Chrome			Hex. Chrome			Copper			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	0.85	0.34	0.68	<0.6	<0.5	<0.8	1.78	1.22	2.38	11.3	15.3	7.71
pH 10	0.08	0.25	0.35	<0.1	<0.3	<0.6	2.89	5.92	11.9	9.21	9.93	6.28

Note: (-) indicates that Cr^{+6} was not determined because Cr^{T} was below the detectable limit.

Table 5-9
Results of Screening Tests for ASTM-A on the Underflow Samples (mg/l)
(Continued)

Plant 6

	Total Chrome			Hex. Chrome			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	0.80	0.06	0.62	0.62	<0.13	0.82	0.20	<0.10	<0.10
pH 10	1.50	1.75	1.75	0.75	2.10	2.05	<0.10	<0.10	<0.10

Plant 7

	Chromium			Cadmium			Copper			Nickel			Zinc		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 7	<.02	.06	.02 .16	<.1	.50	.27 .44	.06	.11	.05 .10	2.75	3.1	2.65 3.90	.68	3.72	2.8 12.0
pH 8.5	<.25	.02 .18	.26	<.02	<.02 .02	<.05	.07	.04 .27	.10	4.25	3.5 2.9	3.34	.99	1.0 .64	.57
pH 10	<.1 <.1	.10	.10	<.02 <.02	<.02	.02	2.44 1.53	.14	.25	20.6 12.8	14.2	1.67	.20 .11	.26	.40

Plant 8

	Total Chrome			Hex. Chrome			Copper			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	0.07	0.05	0.19	<0.05	<0.05	<0.1	0.13	0.18	0.26	0.41	0.33	0.29
pH 10	<0.05	0.45	38.0	<0.05	<0.05	<0.1	0.05	0.14	2.87	0.29	0.33	3.66

Note: (-) indicates that Cr^{+6} was not determined because Cr^{T} was below the detectable limit.

Table 5-10
Results of Screening Tests on Washed Sludge Filtrate (mg/l)

Plant 2	Total Chrome			Hex. Chrome			Cadmium			Zinc		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	<0.10	<0.10	<0.10	<0.05	-	-	3.35	26.7	0.39	0.16	3.10	0.27
pH 10	<0.25	<0.10	0.10	<0.05	<0.05	-	0.02	0.04	0.19	<0.05	<0.05	0.09

Plant 3	Total Chrome			Hex. Chrome			Cadmium		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	3.00	3.05	3.22	2.87	4.32	5.14	0.08	0.12	0.24
pH 10	4.83	4.32	3.68	6.33	3.85	3.72	0.06	0.03	0.17

Plant 4	Total Chrome			Hex. Chrome			Copper			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.50	0.41	0.49	7.12	6.35	3.16
pH 10	0.08	<0.05	<0.05	<0.1	<0.05	<0.05	3.20	2.79	1.64	7.12	2.33	1.14

Note: (-) indicates that Cr^{+6} was not determined because Cr^{T} was below the detectable limit.

Table 5-10
Results of Screening Tests on Washed Sludge Filtrate (mg/l)
(Continued)

Plant 6

	Total Chrome			Hex. Chrome			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	0.17	<0.05	0.05	0.27	–	0.13	<0.10	<0.10	<0.10
pH 10	<0.05	0.18	0.41	–	0.06	<0.10	<0.10	<0.10	<0.10

Plant 8

	Total Chrome			Hex. Chrome			Copper			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	0.05	0.17	12.1	<0.05	<0.05	<0.05	0.18	0.36	1.01	0.19	0.25	1.61
pH 10	0.37	0.21	4.78	<0.05	<0.05	<0.05	0.16	0.20	0.28	0.38	0.32	0.45

Note: (-) indicates that Cr^{+6} was not determined because Cr^T was below the detectable limit.

Table 5-11
Results of Screening Tests for EPA-EP Extract of the Washed Sludge (mg/1)

Plant 2

	Total Chrome			Hex. Chrome			Cadmium			Zinc		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	0.20	1.00	2.30	<0.05	<0.13	0.32	440	425	560	555	625	840
pH 10	3.10	3.10	8.80	<0.13	<0.13	<0.13	510	435	700	630	400	700

Plant 3

	Total Chrome			Hex. Chrome			Cadmium		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	1.74	1.53	0.82	0.07	0.15	0.32	204	311	247
pH 10	1.91	1.70	1.74	0.50	0.04	0.28	154	332	426

Plant 4

	Total Chrome			Hex. Chrome			Copper			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	0.70	0.70	0.86	<0.1	<0.1	<0.25	808	662	873	1110	1090	1030
pH 10	0.11	0.25	1.02	<0.1	<0.05	<0.1	42.8	581	730	234	1250	1560

Note: (-) indicates that Cr^{+6} was not determined because Cr^{T} was below the detectable limit.

Table 5-11
Results of Screening Tests for EPA-EP Extract of the Washed Sludge (mg/l)
(Continued)

Plant 6

	Total Chrome			Hex. Chrome			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	0.56	1.00	2.50	<0.13	<0.13	<0.10	25.0	30.0	42.5
pH 10	0.10	<0.20	1.75	<0.13	-	<0.10	7.44	26.2	43.8

Plant 8

	Total Chrome			Hex. Chrome			Copper			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	429	170	15.2	<0.05	<0.05	<0.6	11.2	4.90	3.40	56.6	39.3	134
pH 10	763	185	18.3	<0.05	<0.05	<0.5	15.3	2.21	3.18	118	64.3	99.9

Note: (-) indicates that Cr^{+6} was not determined because Cr^{T} was below the detectable limit.

Table 5-12
Results of Screening Tests for ASTM-A on Washed Sludge (mg/l)

Plant 2

	Total Chrome			Hex. Chrome			Cadmium			Zinc		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	<0.10	<0.10	<0.10	-	-	-	2.55	46.6	0.87	0.19	4.70	0.71
pH 10	<0.10	<0.10	0.10	-	-	<0.13	<0.02	0.16	0.12	<0.05	<0.05	<0.05

Plant 3

	Total Chrome			Hex. Chrome			Cadmium		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	2.67	2.29	1.49	2.72	1.53	0.93	0.09	0.11	0.04
pH 10	1.70	1.57	3.30	2.11	1.38	2.84	0.05	0.12	0.14

Plant 4

	Total Chrome			Hex. Chrome			Copper			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	0.41	0.14	1.03	<0.5	<0.5	<0.6	1.16	0.62	2.43	9.18	12.4	4.39
pH 10	3.82	0.38	0.25	<0.1	<0.3	<0.3	2.25	2.75	1.61	5.16	4.53	0.84

Note: (-) indicates that Cr^{+6} was not determined because Cr^{T} was below the detectable limit.

Table 5-12
Results of Screening Tests for ASTM-A on Washed Sludge (mg/l)
(Continued)

Plant 6

	Total Chrome			Hex. Chrome			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	0.75	<0.10	0.88	0.30	<0.10	1.00	<0.10	<0.10	<0.10
pH 10	0.62	1.75	2.00	0.70	2.38	2.70	<0.10	<0.10	<0.10

Plant 8

	Total Chrome			Hex. Chrome			Copper			Nickel		
	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3	CaO	NaOH	Na2CO3
pH 8.5	<0.05	0.41	0.33	<0.05	<0.05	<0.1	0.09	0.13	0.20	0.33	0.31	0.29
pH 10	9.46	0.33	22.9	<0.05	<0.05	<0.1	1.46	0.07	1.75	1.73	0.43	2.58

Note: (-) indicates that Cr^{+6} was not determined because Cr^{T} was below the detectable limit.

Table 5-13

Plant 7. Analytical Restults from Leaching Tests, at pH 8.5

	(mg/l) Cd	Cr	Cu	Ni	Zn
(a) Effluent					
CaO	<0.04	0.20	0.03	3.42	0.78
Na_2CO_3	0.01	0.30	0.06	4.20	0.62
NaOH	0.01	0.50	0.06	2.45	1.40
(b) Filtrate, Unwashed Sludge					
CaO	<0.01	<0.05	0.02	2.20	0.02
Na_2CO_3	0.02	0.40	0.04	3.92	1.25
NaOH	<0.01	<0.05	0.04	1.98	0.02
(c) EPA-EP, Unwashed Sludge					
CaO	0.69	0.40	0.16	52.4	90.0
Na_2CO_3	0.19	4.70	0.36	94.4	220
NaOH	0.69	0.40	0.09	64.5	95.0
(d) EPA-EP, Washed Sludge					
CaO	1.00	1.20	0.26	85.0	120
Na_2CO_3	2.80	5.15	0.37	120	255
NaOH	1.25	0.85	0.15	101	175
(e) ASTM-A, Unwashed Sludge					
CaO	0.44	<0.20	2.16	1.50	1.22
Na_2CO_3	<0.04	<0.20	0.02	2.00	0.34
NaOH	<0.05	<0.25	0.10	2.12	0.12
(f) ASTM-A, Washed Sludge (Run in Triplicate)					
CaO	<0.04	<0.25	0.08	2.60	0.38
	0.01	<0.12	0.28	6.06	0.09
	<0.01	<0.12	0.28	6.12	0.10
Na_2CO_3	<0.04	<0.20	0.02	1.70	0.55
	0.02	<0.12	0.16	2.38	0.12
	0.02	<0.12	0.18	2.38	0.08
NaOH	<0.05	<0.20	0.15	1.75	0.16
	<0.01	<0.12	0.08	2.38	0.07
	0.02	<0.12	0.06	2.50	0.06

93 percent and 56 percent. At either pH, the plant's sludge failed the EPA-EP based on cadmium. However, cadmium performed very well during the ASTM-A procedure by not resolubilizing and leaching out, as chromium did. Chromium levels in the plant effluent were more affected by pH than by chemical, while cadmium was affected by both. Results of the EPA-EP testing showed 1000 times higher levels of cadmium to be present than did results of the ASTM-A. Chromium levels did not vary with the two tests and appeared to be independent of chemical, and only slightly dependent on pH.

For Plant 4 at pH 10, chromium was removed from the effluent with an 81 percent efficiency, copper was removed with 84 percent efficiency, and nickel was reduced by 85 percent. Although CaO did not show a clear superiority with the effluent samples, it was most clearly the best overall performer for the EPA-EP and ASTM-A testing. Plant 4 was one of two plants that would have passed the EPA-EP based on these screening tests. At a treatment pH of 10, metal levels in the plant effluent and EPA-EP extracts were always lower when using CaO. It can be seen from Tables 5-8 and 5-9 that although the metals did not resolubilize and leach out during the ASTM-A procedure, the lower pH of the EPA-EP caused considerably higher metals levels in the extract. Metal levels were higher by two orders of magnitude in some cases.

For Plant 6, at pH 8.5 chromium was reduced by 99 percent and nickel by 97 percent in the plant effluent. Chrome in the untreated wastewater was 2 1/2 times higher than nickel although this difference was not evident in the plant effluent. Results of the ASTM-A on the plant sludges shows no significant leaching for either chromium or nickel. During the EPA-EP procedure greater quantities of metals were seen to leach in some cases by as much as 100-fold. The plant's sludge could not be relied upon to consistently pass the EPA-EP. During the first series of tests, all sludge samples passed. However, at pH 8.5 two samples failed during the replication, based on chromium. Best results for the EPA-EP was obtained with treatment at pH 10.

For Plant 7, it can be calculated that at pH 8.5 more than 97 percent of the cadmium has been removed by treatment. It is also evident that the cadmium has not resolubilized and leached out of the sludge during the ASTM-A procedure. Copper was removed from the effluent at approximately a 95 percent efficiency. With the exception of the lime test at pH=10, the copper found in the ASTM-A extract did not resolubilize to a large extent. The exception noted leached at a concentration three to four times higher than the copper concentration in the untreated water. Note that chromium, nickel, and zinc were present in much higher quantities in the untreated wastewater than were cadmium and copper. Chromium was removed from the water at approximately a 98 percent efficiency regardless of chemical or pH. The quantity leached, as measured by the ASTM-A extraction procedure, tended to decrease as the pH of the treatment increased. The removal of nickel from the wastewater is very obviously dependent on pH and only slightly dependent on treatment chemical with NaOH performing somewhat more effectively than CaO or N_2CO_3 as pH increased. Removal rates were approximately 90 percent at pH=8.5. Nickel levels in the sludge leachate were affected by both pH and treatment chemical. At a treatment pH of 10 both the CaO and NaOH generated sludges leached very high levels of nickel while the Na_2CO_3 sludge leached less by a factor of 10. Zinc removal from the wastewater approached 98 percent with little difference between chemicals and minimal pH effects. Sludge leaching results were mixed with respect to treatment chemicals but showed definite reductions in zinc levels as the pH of the treatment was increased.

During the screening tests for Plant 7, the EPA-EP was not performed. Instead, a series of leaching tests performed on larger batch samples prepared at the pH value which gave best results with each treatment chemical during the screening tests were conducted, the results of which are shown in Table 5-13. In the leaching tests, as with the screening tests for this plant, none of the metals seemed to resolubilize and leach out of the sludge during the ASTM-A procedure. Metal levels in the EPA-EP are, as with the other plants, generally higher than the ASTM results but the plant would have passed the EPA-EP.

In order to derive a measure of the statistical significance of these Plant 7 large batch test results, the ASTM procedure was applied to washed sludge precipitated by each of the three chemicals a total of three times. This replication provided the ability to calculate the experimental variation due to chance alone. The test for statistical significance is based on the ratio of the variation in leachate concentration (for each metal) from one treatment chemical to another to the variation due to chance (the F-statistic). Any observed dependence on treatment chemical is significant if this ratio is large enough.

A one-way analysis of variance was performed based on the results presented in Table 5-13. None of the results are significant at the 99 percent level. The dependence of nickel concentration in the leachate on the treatment chemical is significant at the 95 percent level. The effect for no other metal is statistically significant, even at the 90 percent level.

Results for Plant 8 at pH 8.5 shows that chromium was removed by 96 percent, copper by 97 percent, and nickel by 96 percent from the untreated wastewater. Best results for plant effluent was obtained when using CaO. The use of Na_2CO_3 always gave higher metal concentrations in the effluent by at least 10-fold over the CaO results. The ASTM-A procedure did not cause the metals to resolubilize and leach out as did the EPA-EP. The sludge from this plant failed the EPA-EP on the basis of chromium. Although the sludge would still have failed the EPA-EP, less chromium leaching occurred when treatment was with Na_2CO_3. If nickel was ever to be considered a hazardous material under RCRA, the use of Na_2CO_3 for treatment would need to be more thoroughly investigated as it works better for some metals and worse for others.

It should be remembered that direct comparisons between the EPA and ASTM-A extraction procedure test results cannot be made due to the differences in the amount of dilution water used in the respective tests. In the tests done during this part of the study, the EPA-EP extracts had a much higher water-to-solids ratio than the ASTM-A tests and were it not for the differences in pH of the two tests, one would therefore expect lower metal levels in the EPA-EP tests. Comparing EPA and ASTM results in Table 5-13, will demonstrate the significant effect of pH.

Comparing the analytical results of plant effluent and sludge filtrate presented in Tables 5-6, 5-7 and 5-13 shows that in many instances the sludge's interstitial water (filtrate) had metal levels lower than the effluent. This is not as unreasonable as it may initially appear. The kinetics of the precipitation reaction, while initially quite fast, are very slow to reach equilibrium--the point at which precipitation essentially stops. The interstitial waters are in direct contact with the sludge particles for a longer time than the effluent waters and therefore have more opportunities to take advantage of nucleation sites for precipitation. The net result being a lower level of metals in the interstitial water. This theory is reinforced by the observation that the filtrate from the washed sludges had metal levels lower than the filtrate from unwashed sludge. We can assume that equilibrium had not yet been reached.

An unexpected observation was seen in Tables 5-8, 5-11 and 5-13 such that for most cases cadmium and zinc levels in the EPA-EP extract were higher with the washed sludges than with the unwashed sludges. Chromium and nickel levels were generally lower in the EPA-EP extract of the washed sludge than with the unwashed sludges. It had been assumed that washing with deionized water would flush out the high metal levels expected to be found in the interstitial water. Similar mixed results were obtained for washed and unwashed sludges during the ASTM-A extraction where pH is not maintained. This seems to indicate that this phenomenon is not pH related.

It is apparent that washing sludges has no benefit from a leachability standpoint, and may actually cause higher leaching if the sludge contains cadmium.

Certain observations appeared for one plant but could not be broadly applied to others in this study. An example of this comes from Plant 7. The data for this observation comes from Tables 5-8, 5-11, and 5-13. In every case except the unwashed cadmium sample, the sludges generated by Na_2CO_3 had higher metal levels in the EPA-EP extract than did those produced by CaO or NaOH. This effect was especially notable for chrome and zinc. These and other observations, however as mentioned above, could not be applied to other plants in the study and will not be discussed further.

The effect of treatment chemical and pH on the solids content of the sludges is shown in Table 5-14. Calcium oxide, in general, resulted in treated wastewater streams with a higher total solids (TS) content while NaOH resulted in the lowest TS. For CaO, the TS also tended to increase directly with pH, as did Na_2CO_3 while TS was basically unaffected by pH for NaOH. As can be seen for Plant 7 where three treatment pH's were studied, with CaO and NaOH the suspended solids (SS) reached a maximum at pH=8.5 and then dropped off as the pH was increased to 10. SS increased with pH for Na_2CO_3.

5.3 DEWATERING TESTS

5.3.1 TEST PLAN

Batch tests were run using each of the three treatment chemicals considered in the screening test. Larger batches were needed to allow for an evaluation of the effect the chemicals have on the dewaterability of the sludges generated. To reduce the total number of tests to be run, the results of the screening tests were used to select the optimal pH associated with each treatment chemical. Selection of the pH to use was based on a combination of the total metals in the effluent and sludge extract.

Table 5-14

Solids Content of the Screening Test Sludges[a]

(mg/l)

	Plant 2	Plant 3	Plant 4	Plant 6	Plant 7	Plant 8
CaO - pH 7					4015 (2638)[c]	
CaO - pH 8.5	8300	7770	11,000	26,000	4415 (3754)[c]	10,300
CaO - pH 10	7250	9980	28,800	37,800	5230[b] (3520)[c]	7790
NaOH - pH 7					3840 (1945)[c]	
NaOH - pH 8.5	7170	7500	10,100	41,300	3740[b] (2395)[c]	7470
NaOH - pH 10	8740	5250	14,100	25,200	3750 (1940)[c]	8200
Na_2CO_3 - pH 7					3785[b] (1900)[c]	
Na_2CO_3 - pH 8.5	9810	6850	12,100	15,600	3895 (2116)[c]	6900
Na_2CO_3 - pH 10	11,000	6170	16,900	28,000	5420 (2410)[c]	8600

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[a] All values are Total Solids in mg of dried solids per liter of sludge, unless otherwise noted.

[b] Average of replicates.

[c] Suspended solids in mg/l.

Because of the small volume of underflow available, it was necessary to use a small filter apparatus. A 2.54 cm (1.0 inch) diameter circular filter was used with Gelman™ extra thick glass fiber pads as the filter medium. No filter aide was used. One-liter samples of underflow were used for each test. The apparatus was submerged for time periods increasing by 30 seconds with each test. The apparatus was then removed from the bath and held upright to drain for one minute. The rates of filtration were calculated for all tests and pH's.

The objective of these tests were to determine which combination of chemicals and pH perform best by yielding a sludge with reduced capacities to leach heavy metals.

5.3.2 RESULTS

5.3.2.1 Centrifuge Tests

Earlier tests[1] on the leachability of metal finishing wastewater treatment sludges indicated that, in general, sludges with a higher solids content performed better on the EPA-EP. The effect on dewaterability of the underflow by the different treatment chemicals is, therefore, worthy of investigation. Centrifuge tests were run on Plant 7 sludge samples, using a laboratory scale centrifuge with a maximum speed of 6000 rpm. Actual speed could not be determined; however, all tests were run at the same setting. Underflow was fed to the centrifuge at a constant rate (5 ml/min) from a stirred graduated cylinder. The centrifuge was operated in an overflow mode. Tests were stopped when solids were visibly being carried over in the centrate. The basket of the centrifuge had a capacity of approximately 80 ml.

Table 5-15 shows the results of this testing. In all cases a substantial reduction in volume was observed; however, even the best centrifuge test generated a sludge which had less than 3 percent suspended solids. Scale up from this centrifuge to a full-scale industrial centrifuge may yield improved dewatering, but these small scale tests do not indicate much promise for centrifugation as a dewatering technique for sludges from this wastewater. It was also noted that a very fine floc had managed to overflow into the receiver on some tests indicating the ossible need for a downstream filter or recirculation loop.

Due to the poor results on these samples, it was decided that the centrifugation tests would not be performed on the remaining plants.

5.3.2.2 Filter Leaf Tests

For all of the underflow samples, a vacuum of 15 inches Hg was reached in less than 30 seconds for each test. No filter aide was used. The apparatus was submerged for the desired time interval, removed from the bath, and held upright to drain for one minute. The rates of filtration are shown in Figure 5-1 for all chemicals. The sludge cake formed on the filter paper was never more than 2 mm thick.

Table 5-15
Results of Centrifuge Testing

Precipitating Agent	Feed Volume (ml)	Centrate Volume (ml)	Percentage of Water Removal	Suspended Solids in Underflow (mg/l)	Suspended Solids in Cake (mg/l)	Rate of Centrate Collection (ml/min)
NaOH	540	394	73	7780	28,800	4.99
Na_2CO_3	526	362	69	5330	17,100	5.03
CaO	500	308	62	4550	11,800	4.97

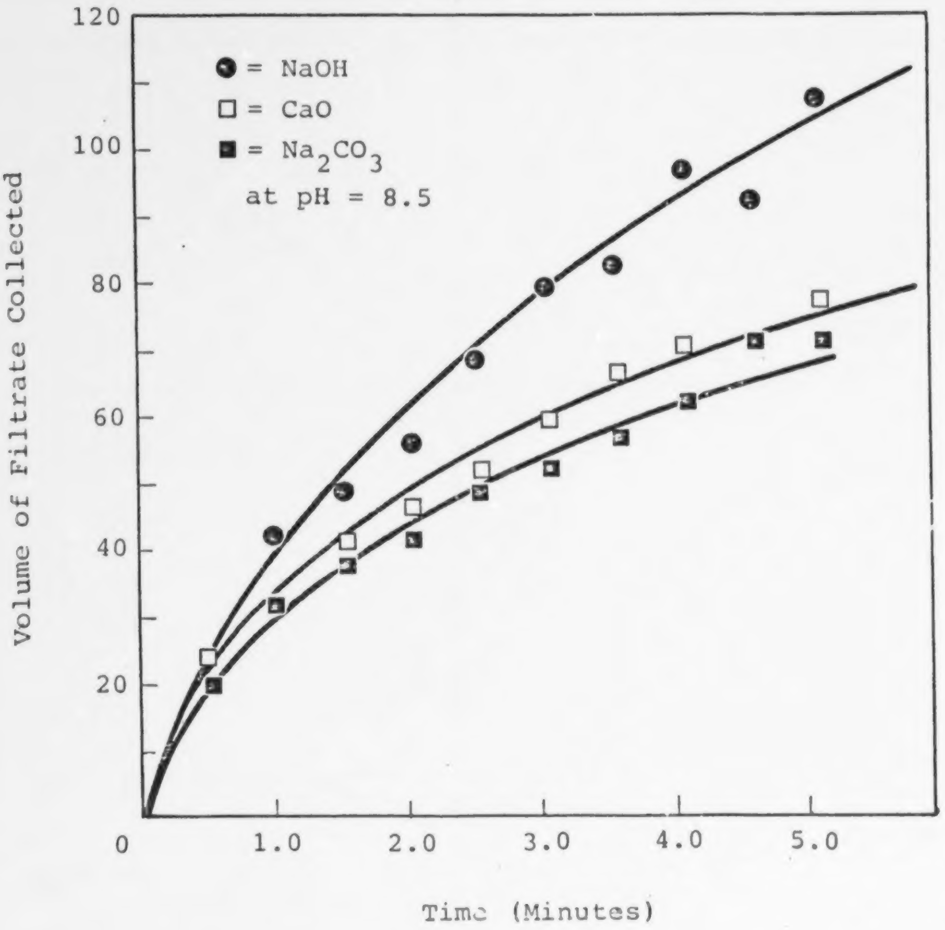

Figure 5-1. Filter Leaf Test Results on Laboratory-Generated Sludges with Plant 7 Wastewater

Filtration rates were calculated for Plant 7 as an example. Over the 5 minute test period, the following average fluxes can be calculated: NaOH, flux = 0.35 ml/cm^2-sec (5.15 gal/ft^2-min); CaO, flux = 0.25 ml/cm^2-sec (3.68 gal/ft^2-min); and Na_2CO_3, flux = 0.23 ml/cm^2-sec (3.39 gal/ft^2-min). Longer tests are needed with a larger supply of underflow to determine the point at which the filter medium becomes essentially plugged. These one-time tests indicate that the NaOH generated sludge from Plant 7's wastewater dewatered by filtration about 40 percent faster than sludges generated by CaO or Na_2CO_3.

5.3.2.3 Aging Tests

The filter leaf tests described in the preceding section were repeated with underflow samples after being treated then allowed to settle for several days. In all instances the filtering properties of the solids were improved. These data are summarized in Tables 5-16 to 5-20.

No conclusions were drawn from these observations. The lack of sample material prevented further study.

Table 5-16
Flocculation Study

Flocculating agent	Manufacturer	Optimum Concentration (mg/l) Plant 2	3	4	6	7	8
Blank	---	poor	poor	poor	poor	poor	poor
Separan AP-273	Dow	poor	poor	1.0*	4.0	1.32*	2.0*
Magnifloc 836A	Cyanamid	2.0*	poor	poor	2.0		poor
L670E	Calgon	poor	poor	poor	poor		poor
WT-3000	Calgon	8.0	NA	4.0	poor		4.0
Separade P-3	Benchmark	---	---	1.5(5)	---	---	---
Percol	Allied Colloids	---	---	---	2.0*(6)	---	---
Floc #306	EPEC	---	---	---	---	---	5.0(5)
Hercofloc	Hercules	---	---	---	---	(0.1)	---

* Indicates flocculating agent and concentration used for each plant's treatment study.

() Indicates approximate concentration used in the plant.

Table 5-17
Plant #3 - Filterleaf Tests
Volume of Filtrate (ml) Collected During Filterleaf Filtration

		Filtration Time (min.)						
	Series	0.25	0.5	1.0	1.5	2.0	3.0	4.0
Fresh Underflow	A	15	16	28	40.5	47	55	68
	B	11	18	27	31	38	59	67
	C	12	19	24	34	41	45	55
	D	5	13	20	21	29	33	44
	E	12	18	25	28	40	44	46
	F	11	15	17	19	30	44	44
Aged Underflow	A	25	40	55	70	90	95	135
	B	25	35	50	65	80	120	120
	C	30	40	55	70	85	125	130
	D	25	55	60	75	100	105	135
	E	35	40	55	65	80	105	115
	F	50	60	75	80	85	105	125

Table 5-18
Plant #4 - Filterleaf Tests
Volume of Filtrate (ml) Collected During Filterleaf Filtration

		Filtration Time (min.)						
Series		0.25	0.5	1.0	1.5	2.0	3.0	4.0
Fresh Underflow	A	85	110	220	230	250	350	440
	B	37	57	96	129	156	205	205
	C	35	-	105	170	215	320	455
	D	35	50	60	115	140	240	240
	E	50	75	125	200	205	305	430
	F	25	40	65	80	95	140	155
Aged Underflow	A	55	85	135	175	210	290	375
	B	35	45	65	75	95	120	145
	*C							
	*D							
	*E							
	*F							

*These samples did not have enough material left to perform this study

Table 5-19
Plant #6 - Filterleaf Tests
Volume of Filtrate (ml) Collected During Filterleaf Filtration

		Filtration Time (min.)						
	Series	0.25	0.5	1.0	1.5	2.0	3.0	4.0
Fresh Underflow	A	25	40	55	60	100	140	230
	B	20	25	40	50	55	65	110
	C	30	40	55	70	85	135	185
	D	20	30	40	50	65	85	150
	E	20	25	40	55	70	85	90
	F	25	30	35	50	50	55	65
Aged Underflow	A	35	35	55	70	85	105	130
	B	20	25	25	35	45	50	55
	C	20	30	35	50	50	65	100
	D	20	30	45	60	75	85	90
	E	30	45	60	65	80	95	105
	F	15	25	35	50	65	70	90

Table 5-20
Plant #8 - Filterleaf Tests
Volume of Filtrate (ml) Collected During Filterleaf Filtration

		Filtration Time (min.)						
Series		0.25	0.5	1.0	1.5	2.0	3.0	4.0
Fresh Underflow	A	25	35	60	80	55	140	165
	B	25	30	50	65	80	110	120
	C	30	50	65	90	90	130	170
	D	20	55	80	110	150	155	265
	E	100	155	150	190	190	200	245
	F	50	60	60	65	100	145	155
Aged Underflow	A	30	35	55	75	80	110	130
	B	25	30	40	50	55	75	85
	C	30	40	60	75	85	115	140
	D	20	35	45	55	65	90	105
	E	150	120	175	170	170	175	190
	F	305	310	300	290	300	300	275

SECTION 6

ANALYSIS OF RESULTS

6.1 STATISTICAL ANALYSIS

Detailed results of the two-way analysis of variance (F-statistic) as applied to the screening tests for each plant (see Section 5 tables) are presented in Section 8. Those results are summarized in Tables 6-1 through 6-3 for the filtrate, effluent, and sludge extract, respectively. Concentrations not assigned a definite value were taken to equal the reported detection limit.

The F-statistic is derived from the ratio of the variation due to the experimental parameters (pH, treatment chemical, and their interaction) to the inherent variation. When this ratio is sufficiently large, the experimental effect observed is determined to be real at a specific level of significance. For instance if the F-statistic (ratio of variations) is sufficiently large to be significant at the 95 percent level, this implies that the experimental result obtained, if due to chance alone, could have occurred only 5 percent of the time. Thus, in such a case, we can be confident at the 95 percent level that the observed effect is real and not due to chance.

The F-statistic was calculated for each of the primary effects, pH, and treatment chemical, and for the interaction effect.

Table 6-1

Values of the F-Statistic

Filtrate

	Plant 2	Plant 3	Plant 4	Plant 6	Plant 8
			(mg/l)		
	Total Chrome				
pH	1.0	6.9*	1.0	0.6	85.3**
Chemical	1.0	.5	1.0	0.4	93.8**
Interaction	1.0	.1	1.0	1.2	77.1**
	Hex Chrome				
pH		.6			
Chemical		1.3			
Interaction		.3			
	Copper				
pH			3.7		.1
Chemical			8.5		17.5**
Interaction			6.0*		6.9*
	Nickel				
pH			8.0*	0.9	11.1*
Chemical			.9	0.9	2.6
Interaction			2.1	1.1	1.9
	Cadmium				
pH	71.1**	13.7**			
Chemical	21.1**	.8			
Interaction	21.8**	.7			
	Zinc				
pH	3.8				
Chemical	1.2				
Interaction	1.7				

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*Significant at 95% level.

**Significant at 99% level.

Table 6-2

Values of the F-Statistic

Effluent

	Plant 2	Plant 3	Plant 4	Plant 6	Plant 7	Plant 8
			(mg/l)			
		Total Chrome				
pH	5.5	2.3	0.0	2.1	11.7*	7.1*
Chemical	5.4*	.1	3.3	2.4	3.7	11.1**
Interaction	5.4*	.1	.6	2.1	3.4	7.4*
		Hex Chrome				
pH		1.8				
Chemical		.1				
Interaction		.3				
		Copper				
pH			2.6		17.6*	307.1**
Chemical			6.9*		1.1	331.3**
Interaction			2.0		3.5	305.3**
		Nickel				
pH			205.2**	0.1	99.4**	38.1**
Chemical			7.1*	3.2	0.2	50.8**
Interaction			6.2*	2.3	0.3	38.4**
		Cadmium				
pH	13.8**	.1			42.5**	
Chemical	1.9	1.7			1.3	
Interaction	4.4	.9			1.0	
		Zinc				
pH	.6				14.7*	
Chemical	2.2				1.1	
Interaction	4.5				3.1	

---

*Significant at 95% level.

**Significant at 99% level.

Table 6-3

Values of the F-Statistic

Sludge - EP

	Plant 2	Plant 3	Plant 4	Plant 6	Plant*** 7	Plant 8
			(mg/l)			
		Total Chrome				
pH	0.2	3.6	2.4	55.2**	3.9	0.1
Chemical	1.4	.9	1.5	9.7	0.8	4.9
Interaction	0.0	0.0	.8	7.5*	2.3	0.1
		Hex Chrome				
pH		3.7				
Chemical		4.6				
Interaction		1.2				
		Copper				
pH			28.0**		3.3	9.0*
Chemical			1.3		2.2	5.0
Interaction			4.1		2.6	4.2
		Nickel				
pH			4.1	7.0*	5.5	.3
Chemical			9.1*	0.3	2.1	17.3**
Interaction			10.8*	3.8	2.1	2.3
		Cadmium				
pH	0.9	2.5			0.3	
Chemical	0.9	5.7*			0.3	
Interaction	0.2	4.0			0.1	
		Zinc				
pH	0.2				0.8	
Chemical	1.8				0.3	
Interaction	1.3				0.3	

---

*Significant at 95% level.

**Significant at 99% level.

***ASTM

Those effects which are significant at the 95 percent level are denoted by a single asterisk, while those meaningful at the 99 percent level have a double asterisk.

One observation based on these tables is the fact that the ability to influence extract quality by variation of treatment factors is apparently plant-specific. Table 6-3 shows that for two plants (2 and 7) there were no meaningful effects for any of the metals, whereas for three other plants (4, 6, and 8) a majority of the metals were influenced significantly. The ability to influence extract quality appears also to vary among metals considered. Table 6-3 shows that chrome is significant for only 1 of 6 plants, whereas there is a meaningful effect on the level of nickel in the extract in 3 of the 4 plants (and the 4th is very close to being significant at the 95 percent level). The level of copper in the filtrate, effluent, and sludge extract appears open to influence by the treatment parameters, a meaningful effect being revealed for every experiment performed with copper except for the Plant 7 ASTM extract (see Tables 6-1 through 6-3). Zinc, on the other hand, showed a real effect in only one of five experiments.

It is not clear that either pH or treatment chemical can be said in general to be the more significant controlling variable--often real interaction effects are shown. But this conclusion clearly depends on the particular plant; in the case of Plant 7, pH had a real effect for all five metals in the effluent while the treatment chemical never showed a real effect.

In order to test for for overall (all plants) significance of the main effects (pH and chemical) and their interaction, the Pearson P [1] statistic was calculated, where

$$P = -2 \quad \ln P_i$$

and P_i is the probability for the ith plant of obtaining a value of F greater than or equal to the value actually observed. P is distributed as Chi-square with 2k degrees of freedom, where k is the number of independent tests (or plants, in this case). Plant 7 entered into these calculations for only the effluent, since neither filtrate data nor EP extract data was obtained during the designed experiment for that plant.

The following table shows that this test indicates that a number of overall effects are significant at the 0.95 level, about double the number of significant effects for effluent and for filtrate as for EP extract. But these results must be interpreted carefully in light of the single plant results. The P test requires that the independent experiments contributing to the statistic be homogeneous, whereas the plants selected for this study were chosen because each performs different types of plating. There may be real reasons why some effects are extremely significant at some plants and not at others. A test for overall significance may therefore be of questionable worth.

---

[1] Rao, C. D., Advanced Statistical Methods in Biometric Research, John Wiley & Sons, New York, 1952 (pp 217-222).

Values of the P Statistic

	Chromium	Copper	Nickel	Cadmium	Zinc
		Effluent			
pH	25.5*	37.3*	51.0*	19.9*	8.7
Chemical	27.4*	37.1*	29.3*	7.5	4.9
Interaction	21.6*	34.4*	26.2*	8.3	8.8
		Filtrate			
pH	30.7*	5.1	17.2*	26.8*	(1)
Chemical	26.0*	19.6*	13.8*	13.9*	(1)
Interaction	25.4*	13.8*	8.0	13.9*	(1)
		Sludge Extract (EP)			
pH	25.5*	20.0*	12.4	5.5	(1)
Chemical	20.8*	8.0	20.4*	8.0	(1)
Interaction	9.1	10.4*	17.5*	5.5	(1)

---

*Significant at 0.95 level.

(1) not applicable - data for zinc from a single plant.

6.2 ANALYSIS OF EFFECTS ON EFFLUENT QUALITY

Effluent quality studies on plant wastewater were performed as described in Section 5.2, Screening Tests. Analytical results from these tests (Table 5-6) were compared to the analysis of combined untreated wastewater (Table 5-3) so that an evaluation could be made as to which combination of chemicals and pH was performing best, based on effluent quality and sludge leaching characteristics. Metal removal efficiencies without averaging replicates are shown in Table 6-4 for the six plant effluents.

The levels of cadmium and zinc in Plant 2 wastewater were greatly reduced at pH 10 especially with CaO and NaOH precipitation.

Table 6-4
Metal Removal from Effluent %

Plant	Treatment	Cd	Cr	Cu	Ni	Zn
#2	CAO pH 8.5	80	100	-	-	98
	CAO pH 10.0	100	100	-	-	99
	NAOH pH 8.5	75	100	-	-	98
	NAOH pH 10.0	99	99	-	-	99
	Na_2CO_3 pH 8.5	97	100	-	-	99
	Na_2CO_3 pH 10.0	97	98	-	-	98
#3	CAO pH 8.5	94	62		-	-
	CAO pH 10.0	98	47		-	-
	NAOH pH 8.5	79	61		-	-
	NAOH pH 10.0	89	38		-	-
	Na_2CO_3 pH 8.5	90	59		-	-
	Na_2CO_3 pH 10.0	81	47		-	-
#4	CAO pH 8.5	-	85	81	69	-
	CAO pH 10.0	-	71	97	89	-
	NAOH pH 8.5	-	94	87	50	-
	NAOH pH 10.0	-	94	89	85	-
	Na_2CO_3 pH 8.5	-	67	71	61	-
	Na_2CO_3 pH 10.0	-	71	74	82	-

Table 6-4
Metal Removal from Effluent %
(Continued)

Plant	Treatment	Cd	Cr	Cu	Ni	Zn
#6	CAO pH 8.5	-	99	-	97	-
	CAO pH 10.0	-	100	-	99	-
	NAOH pH 8.5	-	100	-	97	-
	NAOH pH 10.0	-	100	-	99	-
	Na_2CO_3 pH 8.5	-	99	-	96	-
	Na_2CO_3 pH 10.0	-	76	-	89	-
#7	CAO pH 8.5	94	98	92	88	98
	CAO pH 10.0	94	98	90	96	97
	NAOH pH 8.5	97	98	95	93	98
	NAOH pH 10.0	97	98	90	95	98
	Na_2CO_3 pH 8.5	97	98	97	89	98
	Na_2CO_3 pH 10.0	94	97	90	94	97
#8	CAO pH 8.5	-	100	98	99	-
	CAO pH 10.0	-	99	98	98	-
	NAOH pH 8.5	-	100	98	99	-
	NAOH pH 10.0	-	99	98	98	-
	Na_2CO_3 pH 8.5	-	84	94	87	-
	Na_2CO_3 pH 10.0	-	41	7	0	-

Greater than 98 and 99 percent of the cadmium and zinc, respectively, has been removed by treatment. The chromium content was reduced to below the detection limit which was by all treatments except Na_2CO_3 at pH 10.

High chromium levels in Plant 3 effluent are a major problem. Analysis of the effluent for Cr^{+6} suggests the reason for this problem lies in ineffective Cr^{+6} reduction. Hexavalent chromium is much more soluble (and therefore more difficult to precipitate) than trivalent chromium. The plant sample corresponding to "yellow Cr-treated (L2)" (Table 4-1) had a pH of 12.38 and had a Cr^{+6} level indicating 97 percent of the chromium was hexavalent. Chrome reduction requires low pH and this observation suggests inadvertant addition of alkali without monitoring pH at the plant. Approximately 50 percent of the chromium was found in the plant effluent, mainly as Cr^{+6}. This fact stresses the importance of proper Cr^{+6} reduction pretreatment to control effluent quality. The best effluent quality with respect to cadmium was observed with CaO treatment at pH 10, whereas lower chromium levels were found at pH 8.5 independent of chemicals used. Chromium levels in the filtrate and effluent were very similar. This may be due to a slower rate of precipitation of cadmium than chromium and may also be affected by the anomalous amount of chromium in the more soluble hexavalent state.

The lowest levels of metals in the Plant 4 effluent were obtained with CaO treatment at pH 10. Nickel, the highest metal component of the untreated waste stream was the most difficult to remove. Nickel showed a removal rate of approximately 85 percent. Nickel removal showed a pH effect favoring pH 10. Chromium levels in the effluent and filtrate were low (less than 0.5 mg/l) for all treatment conditions.

Plant 6 was analyzed for Cr^T, Cr(6+) and Ni. A large amount of chromium was in the untreated wastestream. The Cr^{+6} levels were found to be low indicating proper Cr^{+6} reduction pretreatment. As a result low levels of Cr^T and Cr^{+6} were found in the effluent. This contrasts with the high amount of chromium, found in the effluent of Plant 3 where ineffective chromium reduction was observed. Most effective removal rates for nickel were observed at pH 10 with CaO and NaOH treatments. Chromium and nickel were both removed poorly by Na_2CO_3 treatment at pH 10.

The lowest levels of metals in the Plant 7 effluent were obtained with either CaO or NaOH at pH 10. Nickel and zinc, the two highest metal components of the untreated waste stream were also the highest metal components in the effluent. Nickel showed a removal rate of about 95 percent, and Zn about 97 percent. Cadmium which had the lowest metal level in the wastewater, was also the lowest metal component in the effluent. The low concentration of cadmium in the wastewater was partly due to the fact that the wastewater had to be spiked with CdCN solution for it to appear at all. This is further explained in the Plant 7 information in Section 7. Chromium levels in the effluent were low for all treatment conditions. This may be attributed in part to effective Cr^{+6} reduction, similar to Plant 6, as essentially no Cr^{+6} was found in the effluent.

Plant 8 was analyzed for Cr^T, Cr^{+6}, copper and nickel. This wastestream had a very large chromium content. The effective removal of chromium by NaOH and CaO can be attributed in part to effective Cr^{+6} reduction. Essentially no Cr^{+6} was found in the effluent. Treatment of this wastestream with Na_2CO_3 was much less effective than CaO or NaOH. The effluent in the Na_2CO_3 treatment remained cloudy after settling. It seems likely that the major source of high metal content of the effluent in this case is due to poor settling, especially since the filtrate and washed filtrate show much lower metal contents. Copper, chromium and nickel removal exceeded 97 percent for NaOH and CaO treatment with little pH preference.

Zinc was found in the wastestreams in two out of six plants. It was removed from the effluent with greater than 97 percent efficiency with the use of any precipitating chemical at pH 8.5 and 10. Nickel was a component of the wastestreams of four plants. It was consistently removed better (greater than 85 percent) by CaO and NaOH treatments at pH 10. Copper was present in four wastestreams investigated. Lime treatment at pH

10 and NaOH treatment at either pH 8.5 or 10 removed at least 87 percent of this metal. Cadmium was present in three waste streams. It was best precipitated at pH 10 with CaO with 94 percent or better removal. Chromium was a component of all six wastestreams investigated. In the five plants with effective chromium reduction pretreatment, chromium was 85 percent or greater removed by NaOH and CaO treatment at pH 8.5. Where chromium was primarily in the hexavalent form (one plant), the best precipitation was obtained at pH 8.5 and was only about 60 percent effective.

Superior effluent quality was found with precipitation at pH 10 with CaO producing slightly more consistent low levels of metals than NaOH. Soda ash (Na_2CO_3) produced the most variable results with especially poor results at pH 10. It was also found that inordinately large quantities of Na_2CO_3 were required to raise the pH to 10. The adjustment of pH with NaOH was much more rapid than with CaO. In existing plant systems where pH adjustment residence times are very short, NaOH treatment may produce more consistent results. High levels of chromium in the effluent were found where chromium reduction pretreatment was inadequate, otherwise chromium levels were very low.

Results of the screening tests on plant effluent (clarifier overflow) have been plotted and are included in Appendix III.

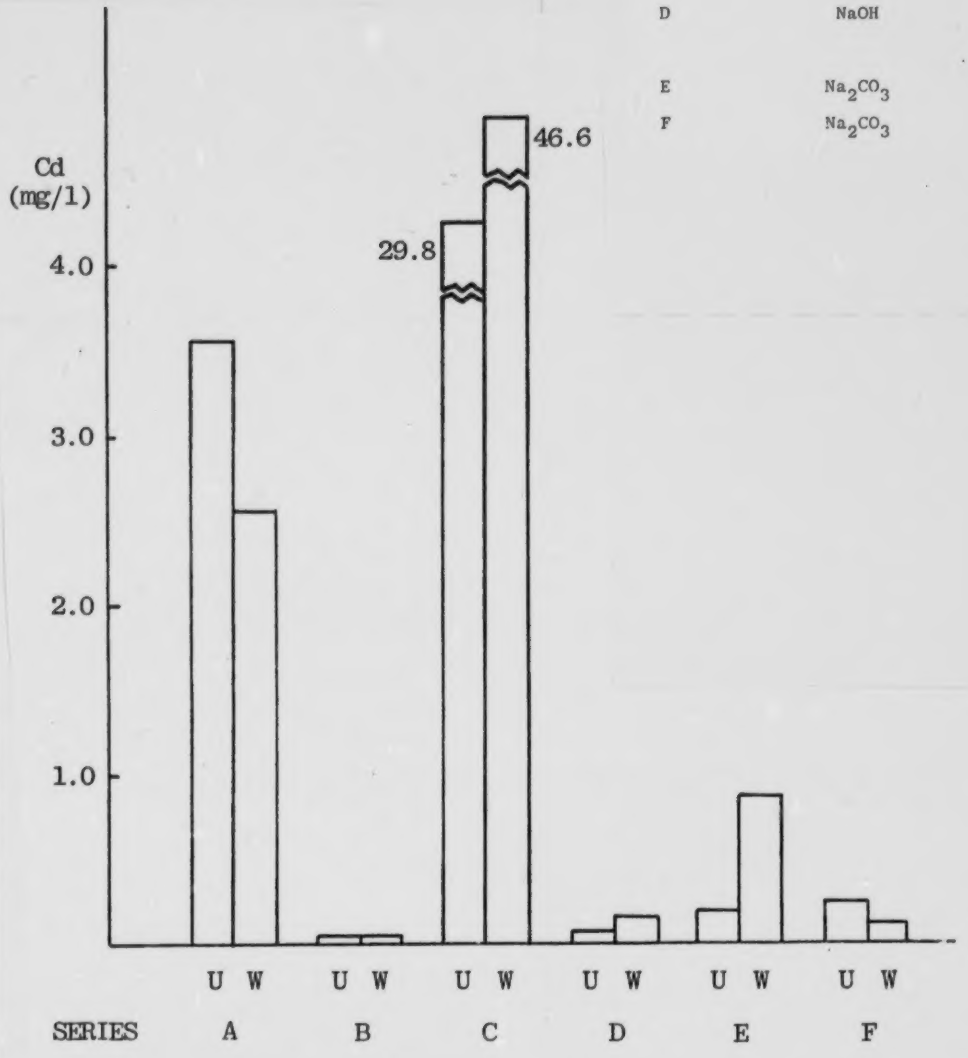
6.3 ANALYSIS OF EFFECTS ON SLUDGE LEACHABILITY

Leachability studies on washed and unwashed sludges were performed using the EPA-EP and the ASTM-A extraction procedures. These extractions differ considerably in that the EPA-EP is conducted using an acidic (pH 5) extraction whereas the ASTM-A procedure is an extraction with deionized water.

The cadmium, zinc and chromium levels in the ASTM-A extracts, Figures 6-1 and 6-2 for Plant 2 washed and unwashed sludges follow the same trends as the washed filtrate and filtrate respectively. Chromium was well stabilized against leaching having values near or below its detection limit (0.10 mg/l). The lowest leachability of metals was observed with CaO and NaOH treatment at pH 10. The lower levels of metals in the ASTM-A extracts appear to be mainly due to a dilution of the interstitial water. The EPA-EP extracts, Figures 6-3 through 6-5, show much higher levels of leaching of these metals due to their increased solubilities at pH 5. Cadmium and zinc levels were high for both washed and unwashed sludges. They exhibited little variability with precipitation chemicals and showed minimal pH effects. The washed sludges leached significantly lower amounts of chromium. Unwashed samples showed a pH effect favoring pH 8.5. Precipitation by Na_2CO_3 resulted in a 10-fold increase in chromium leachability.

In Plant 3, cadmium is readily leached in the EPA-EP extraction, Figures 6-8 through 6-10, while negligible leaching occurs in

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0



Cadmium levels in washed (W) and unwashed (U) sludges extracted by the ASTM Method A extraction procedure for plant # 2.

Figure 6-1. Plant #2 Cd in ASTMs-A

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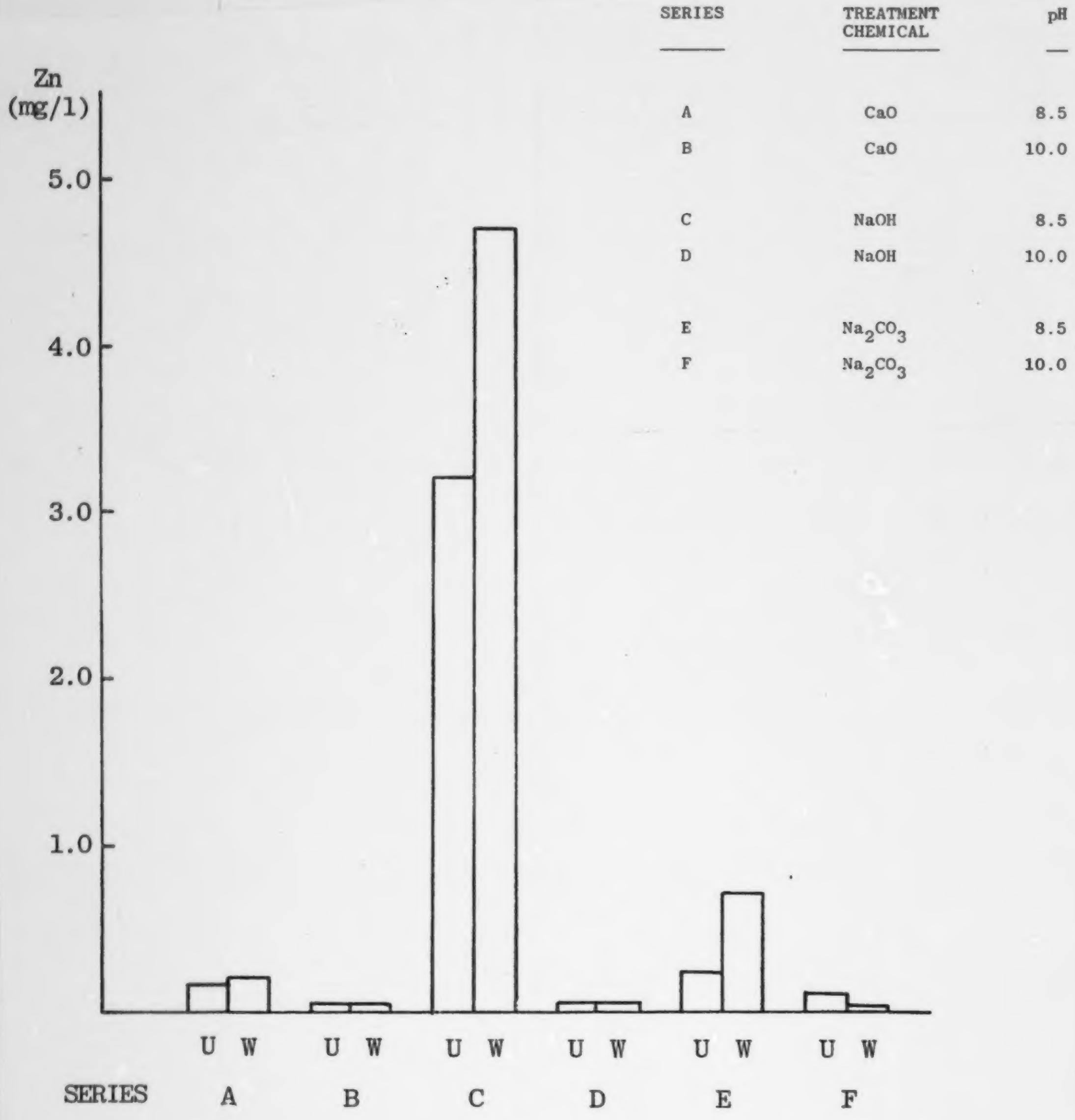

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Zinc levels in washed (W) and unwashed (U) sludges extracted by the ASTM Method A extraction procedure for plant # 2.

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Figure 6-2. Plant #2 Zn in ASTMs-A

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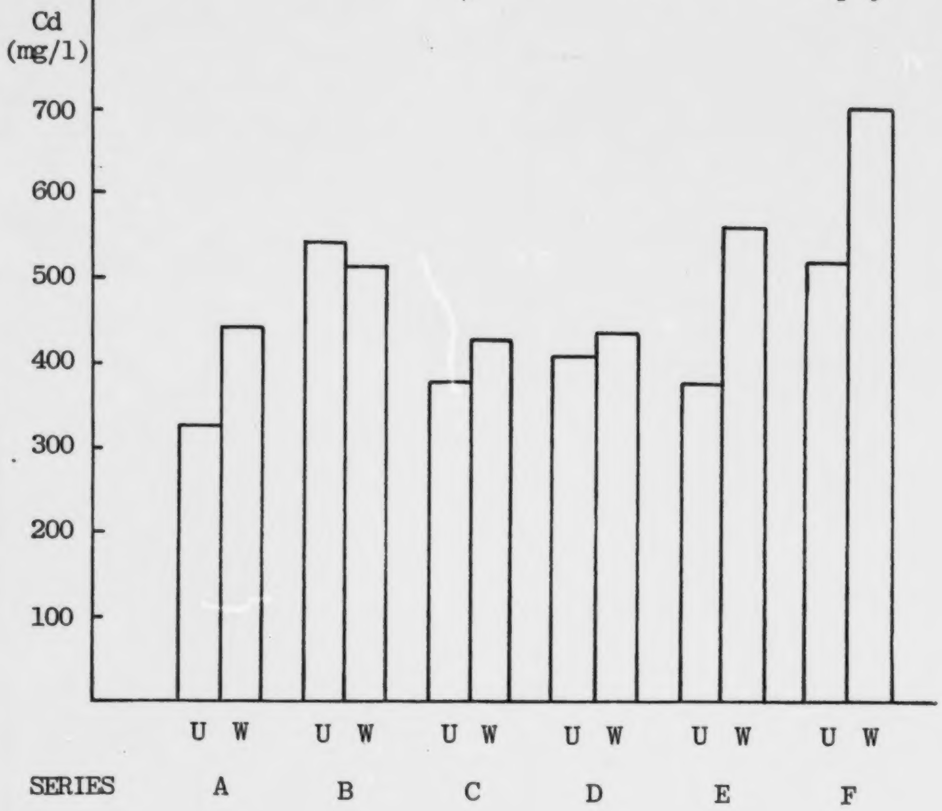
SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0



Cadmium levels in washed (W) and unwashed (U) sludges extracted by the EPA extraction procedure for plant # 2.

Figure 6-3. Plant #2 Cd in EPA-EP

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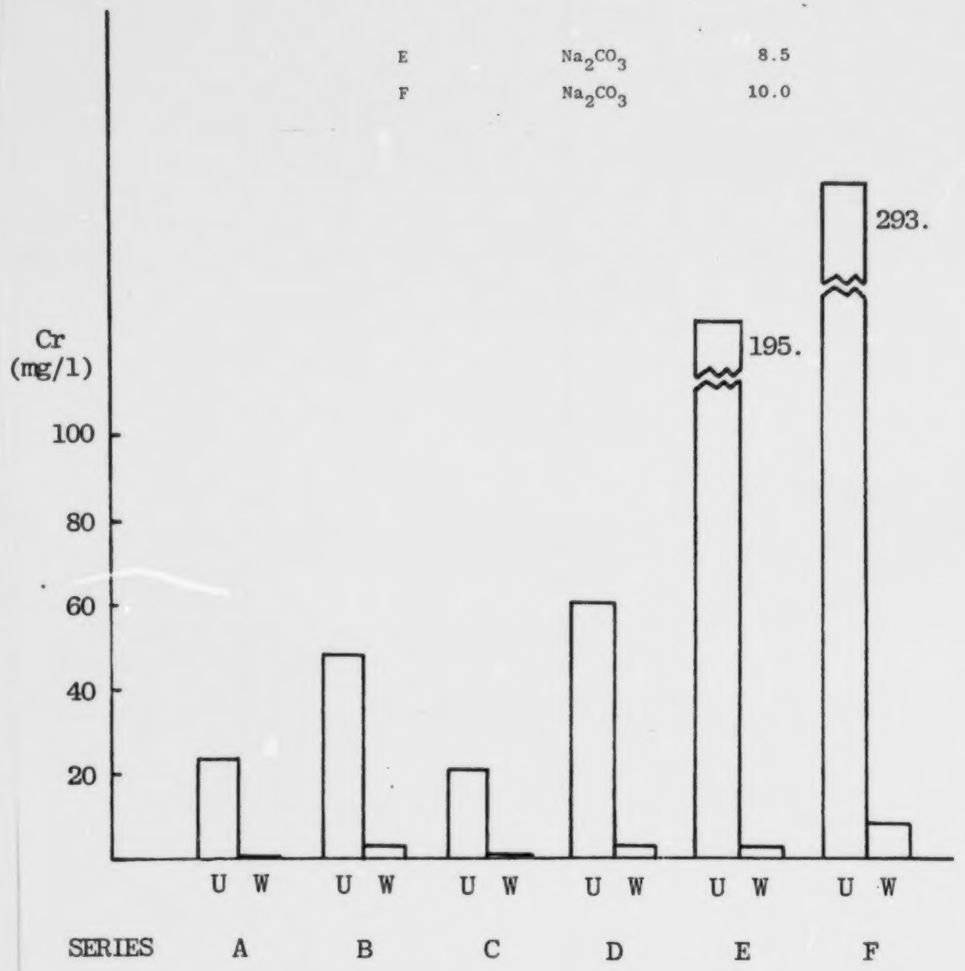
SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Note: Cr^{6+} less than detection limit.



Chromium levels in washed (W) and unwashed (U) sludges extracted by the EPA extraction procedure for plant # 2.

Figure 6-4. Plant #2 Cr in EPA-EP

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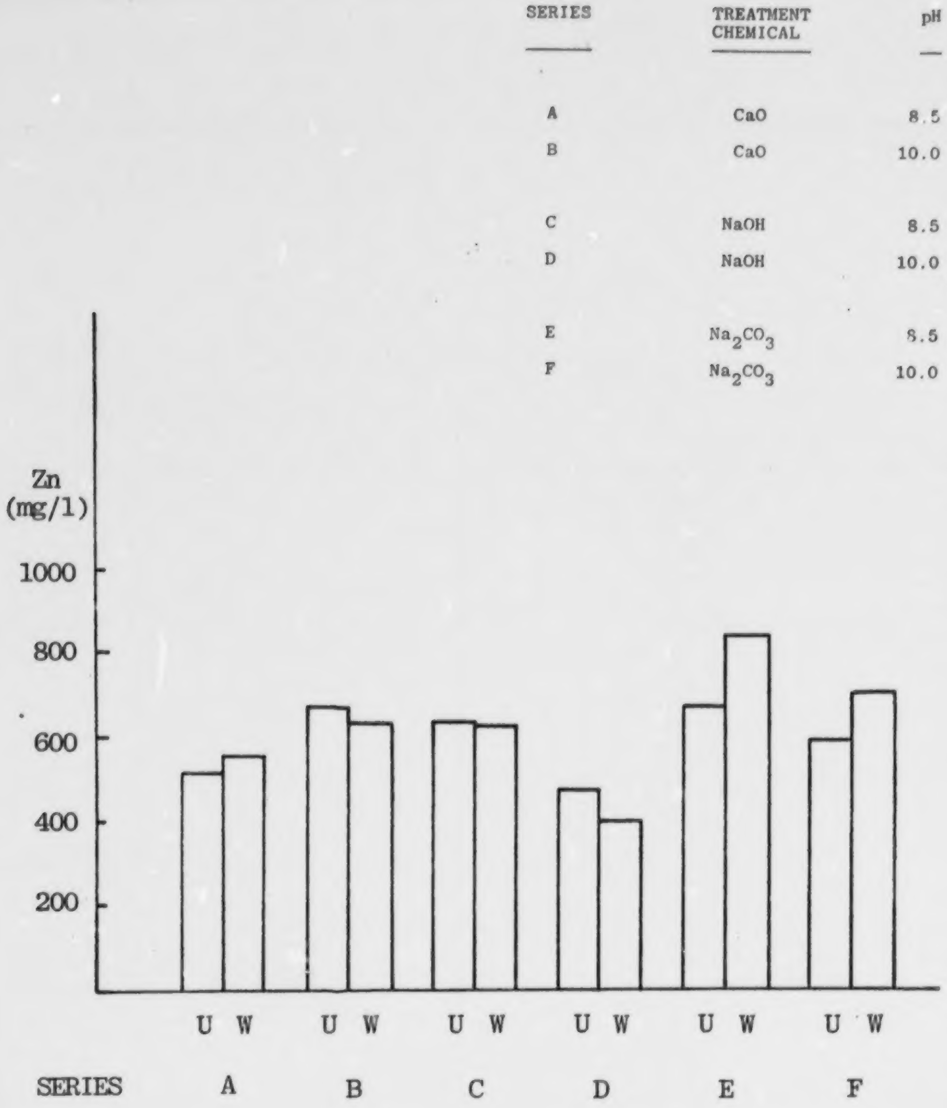

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Zinc levels in washed (W) and unwashed (U) sludges extracted by the EPA extraction procedure for plant # 2.

Figure 6-5. Plant #2 Zn in EPA-EP

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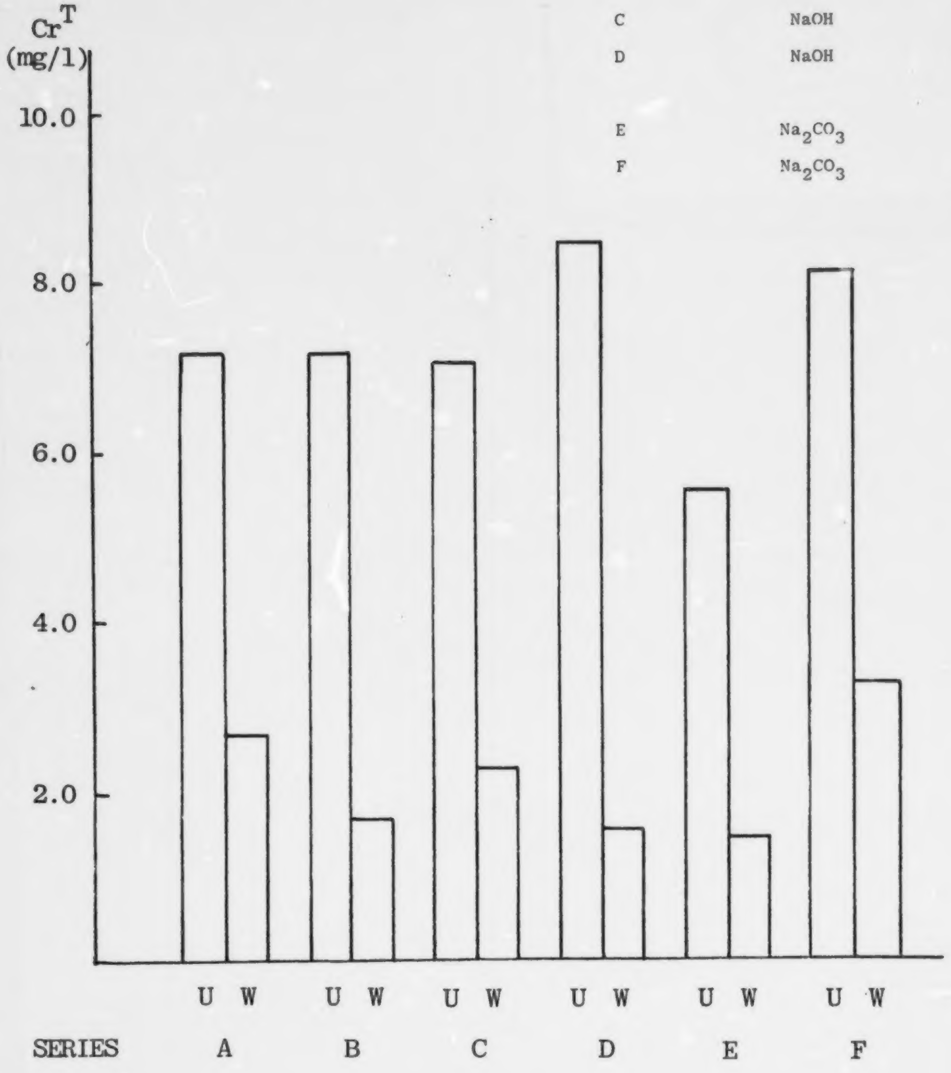
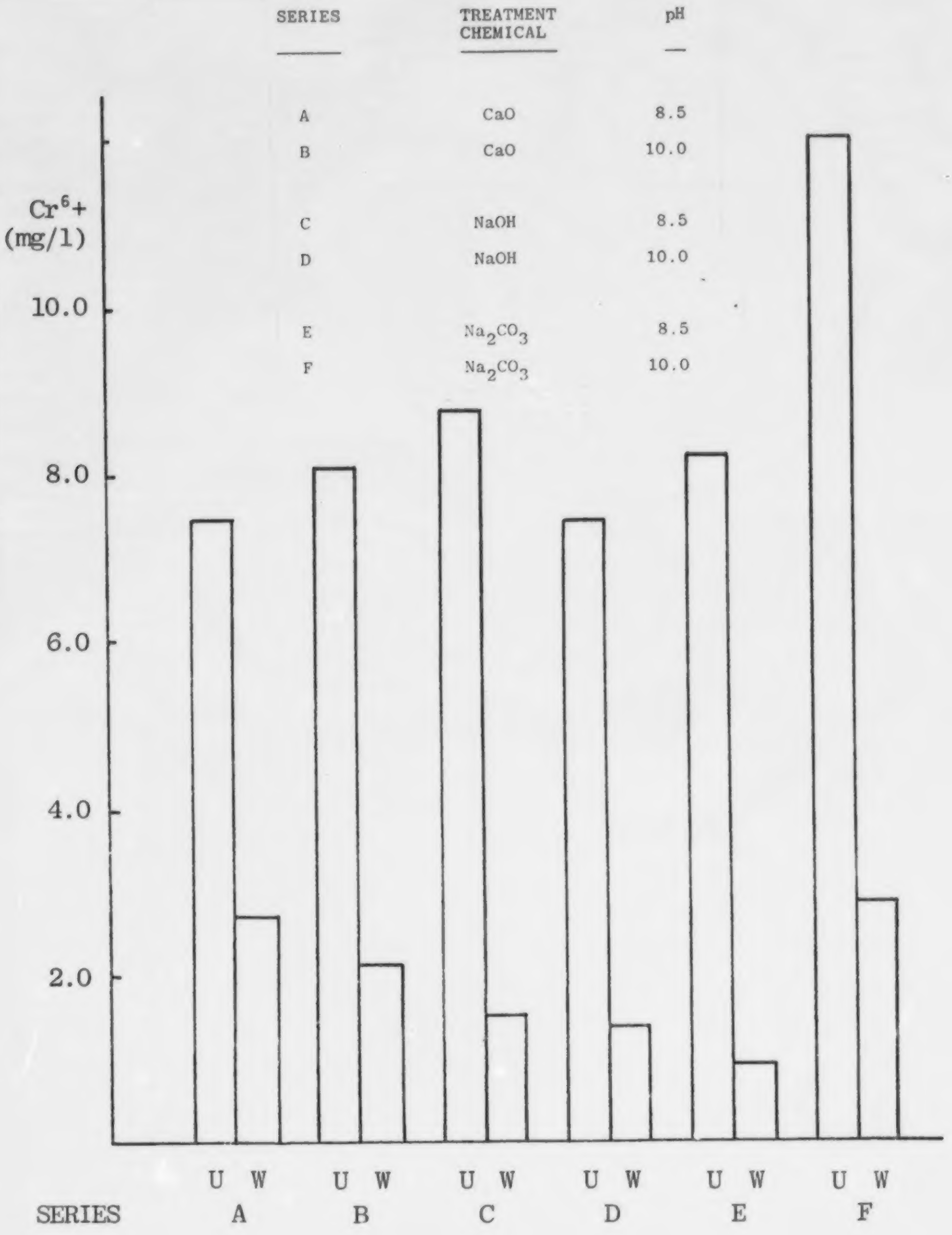
SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0



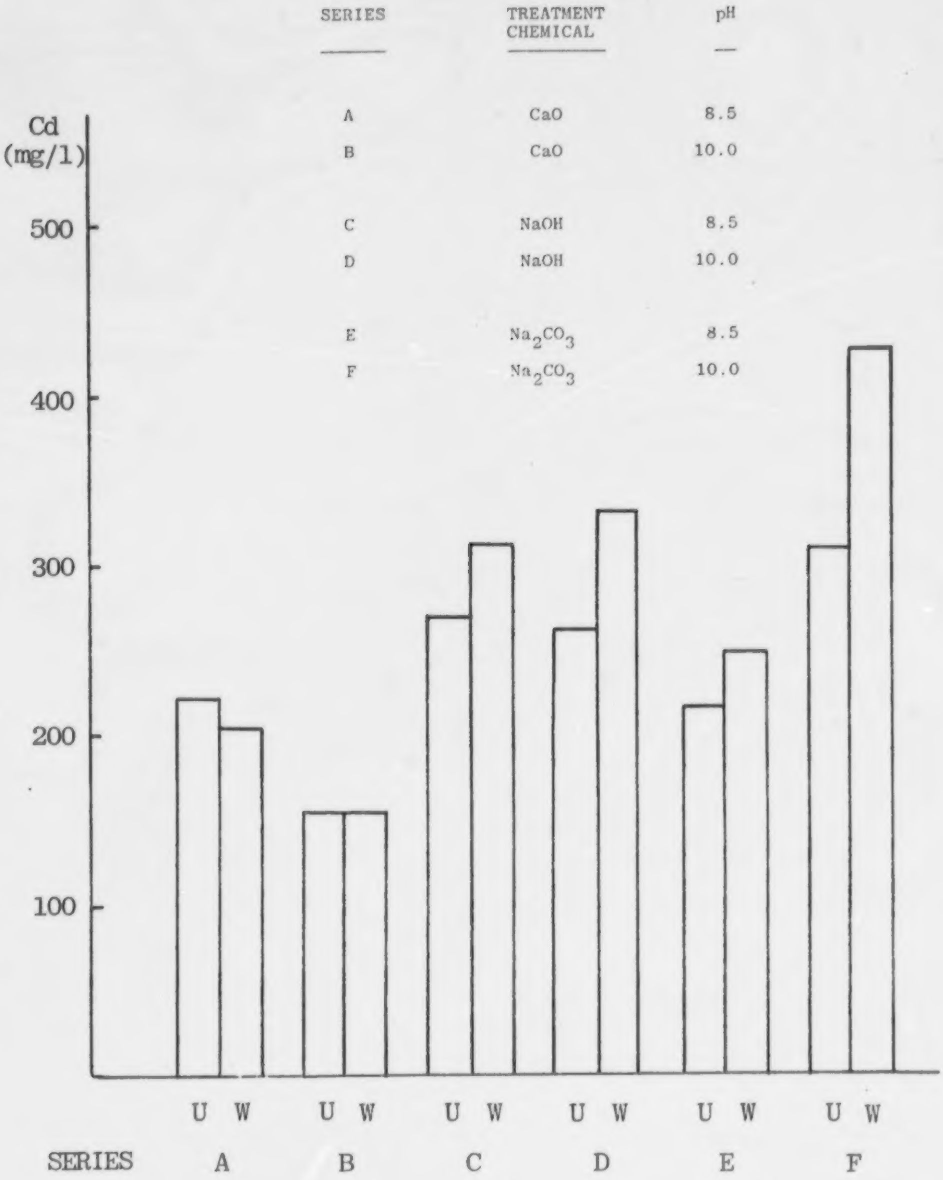
Chromium levels in washed (W) and unwashed (U) sludges extracted by the ASTM Method A extraction procedure for plant # 3.

Figure 6-6. Plant #3 Cr^T in ASTMs-A



Hexavalent Chromium levels in washed (W) and unwashed (U) sludges extracted by the ASTM Method A extraction procedure for plant # 3.

Figure 6-7. Plant #3 Cr^{6+} in ASTMs-A



SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Cadmium levels in washed (W) and unwashed (U) sludges extracted by the EPA extraction procedure for plant # 3.

Figure 6-8. Plant #3 Cd in EPA-EP

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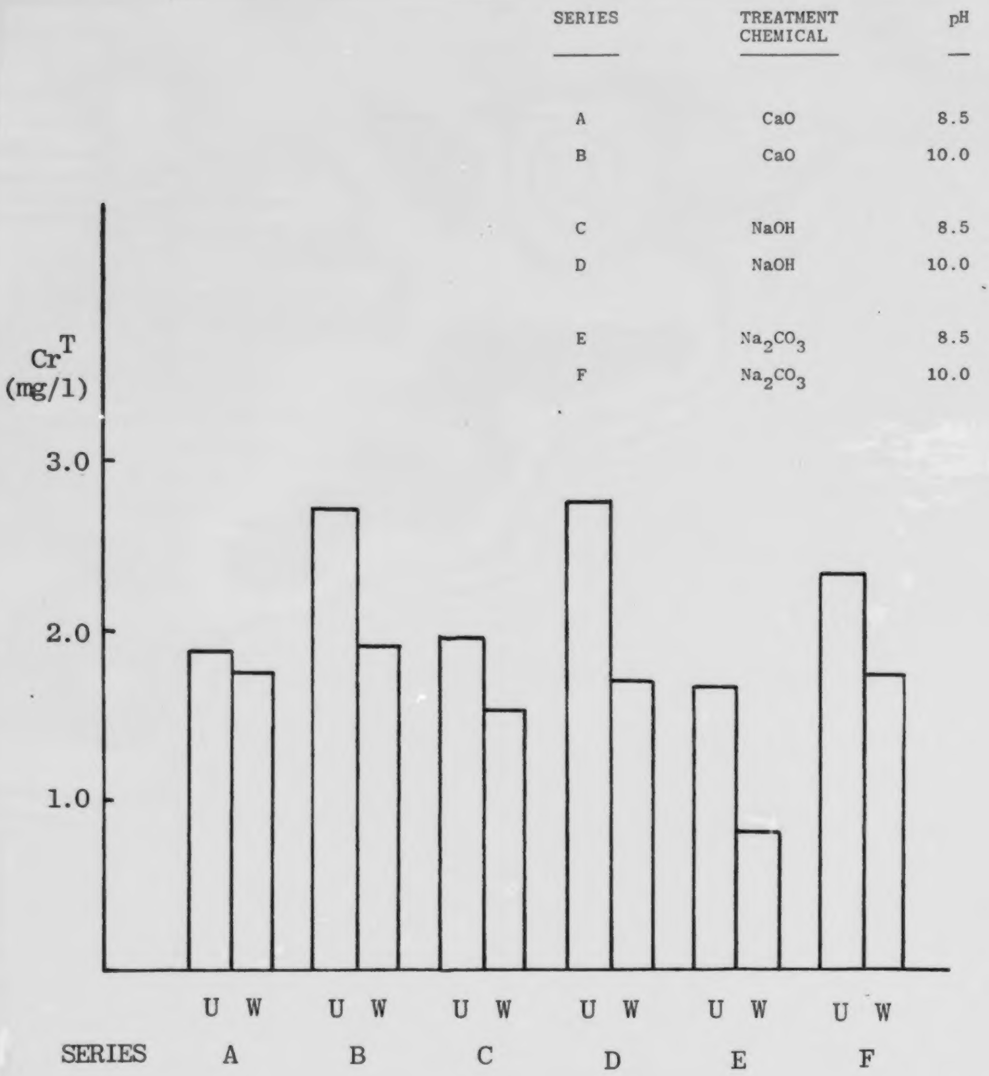

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Chromium levels in washed (W) and unwashed (U) sludges extracted by the EPA extraction procedure for plant # 3.

Figure 6-9. Plant #3 Cr^T in EPA-EP

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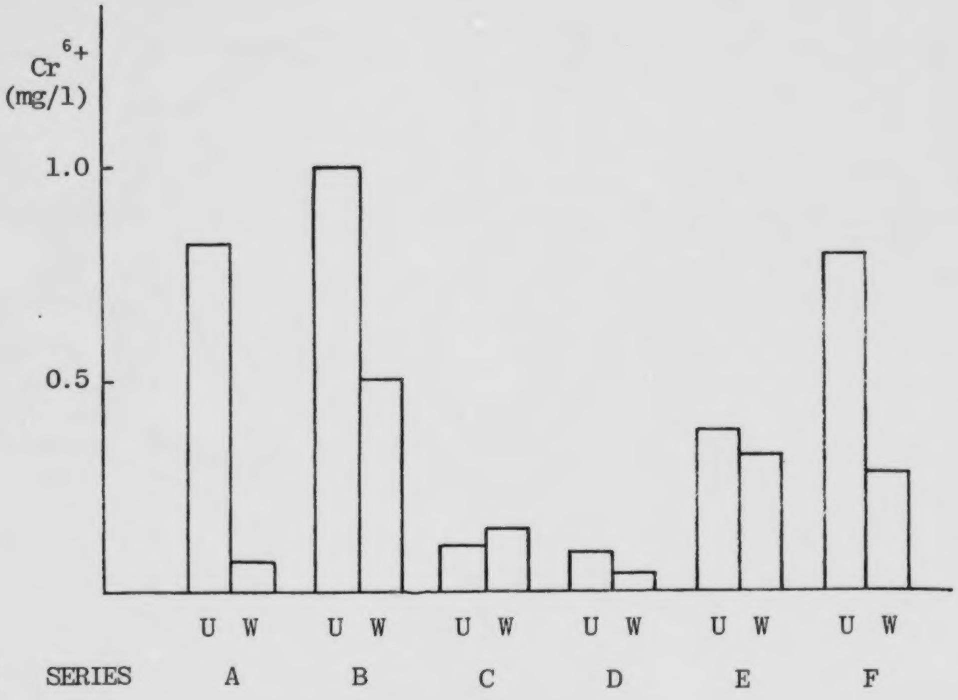
SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0



Hexavalent Chromium levels in washed (W) and unwashed (U) sludges extracted by the EPA extraction procedure for plant # 3.

Figure 6-10. Plant #3 Cr^{6+} in EPA-EP

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the ASTM-A extraction, Figures 6-6 and 6-7 This contrasts with the behavior of chromium. The low leachability of chromium in the EPA-EP extraction compared to the ASTM-A extraction may result from the reduction of Cr^{+6} under the acidic conditions of the EPA-EP extraction.

The most stable sludge generated in Plant 4 experiments may be interpreted in terms of the leachability of copper and nickel, the two predominant metals in the waste stream. Precipitation using CaO at pH 10 greatly reduces the leachability of both of these metals. Chromium leached less than 1.0 mg/l in both ASTM-A and EPA-EP extractions, see Figure 6-12. Lime at pH 10 produces the most favorable levels of metals under the EPA-EP extraction. There is much lower variability in these sludges under ASTM-A extraction conditions.

In Plant 6, the EPA-EP extract of the CaO precipitated sludge at pH 10 shows the lowest levels of nickel, see Figure 6-20. The washed and unwashed sludges extracted by ASTM-A leached very little nickel. Chromium was best stabilized in CaO and NaOH sludges precipitated at pH 10 for the EPA-EP extraction, Figure 6-19, while pH 8.5 proved better for the ASTM-A extraction, Figure 6-17. The chromium extracted by ASTM-A or EPA-EP extractions was below 5 mg/l for all treatments and considerably better for some treatments. It is interesting to note that ASTM-A leached chromium as hexavalent chromium although little or no Cr^{+6} was in the effluent or filtrates. It is unclear

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SERIES	TREATMENT CHEMICAL	pH
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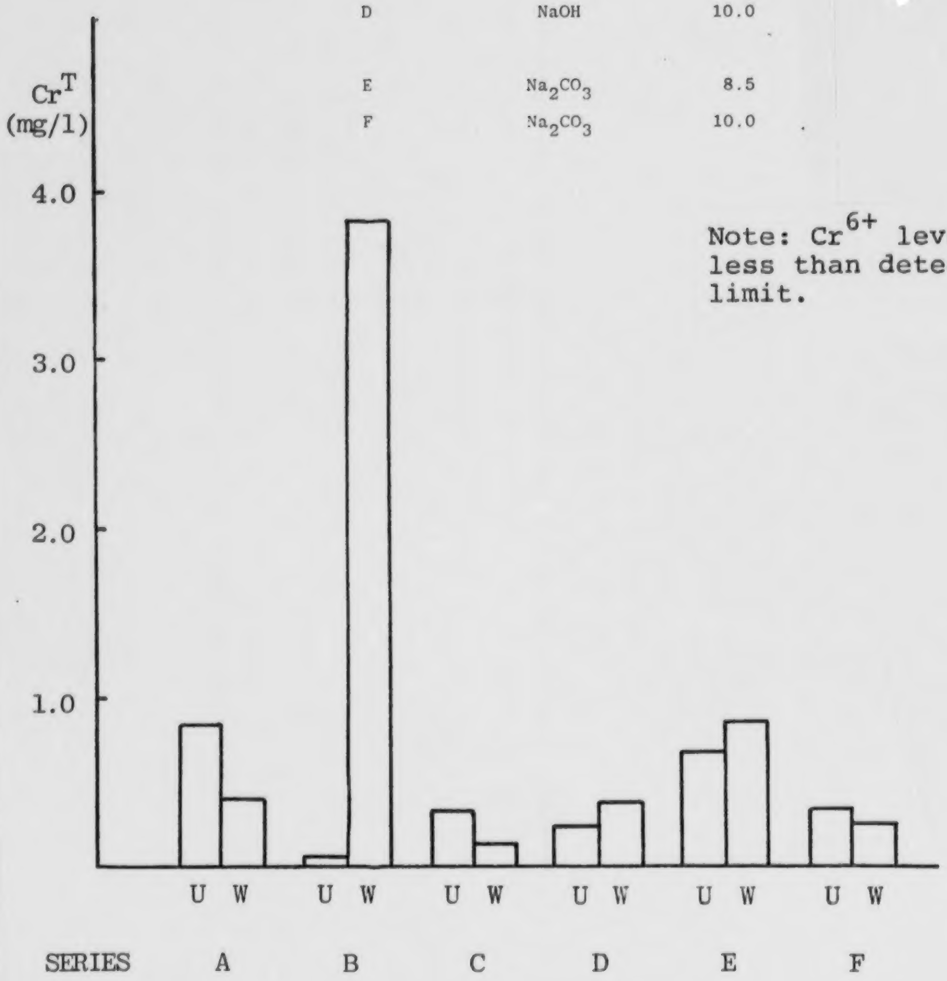
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0



Note: Cr^{6+} levels less than detection limit.

Chromium levels in washed (W) and unwashed (U) sludges extracted by the ASTM Method A extraction procedure for plant # 4.

Figure 6-11. Plant #4 Cr^T in ASTMs-A

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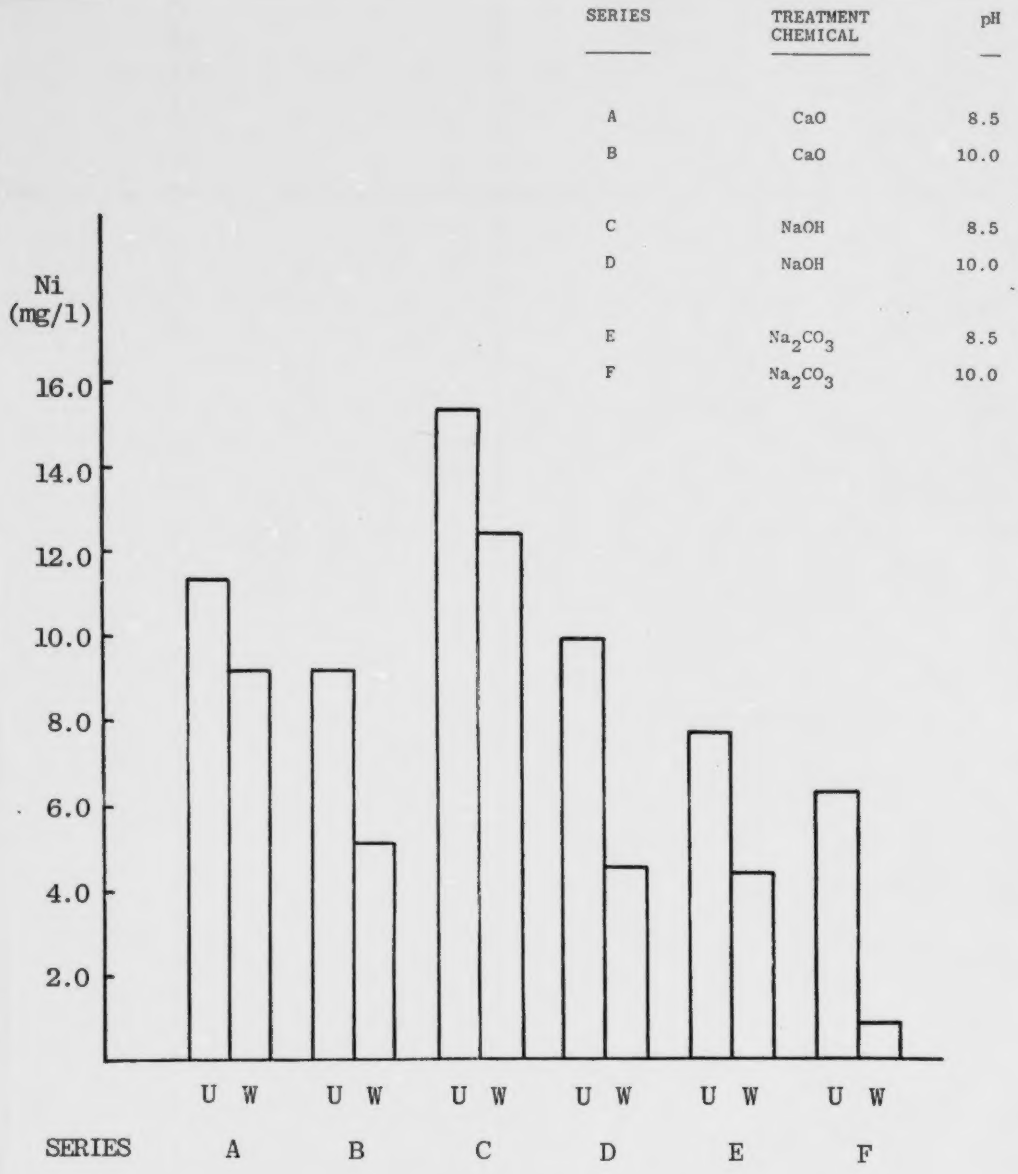

SERIES	TREATMENT CHEMICAL	pH
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B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Nickel levels in washed (W) and unwashed (U) sludges extracted by the ASTM Method A extraction procedure for plant # 4.

Figure 6-12. Plant #4 Ni in ASTMs-A

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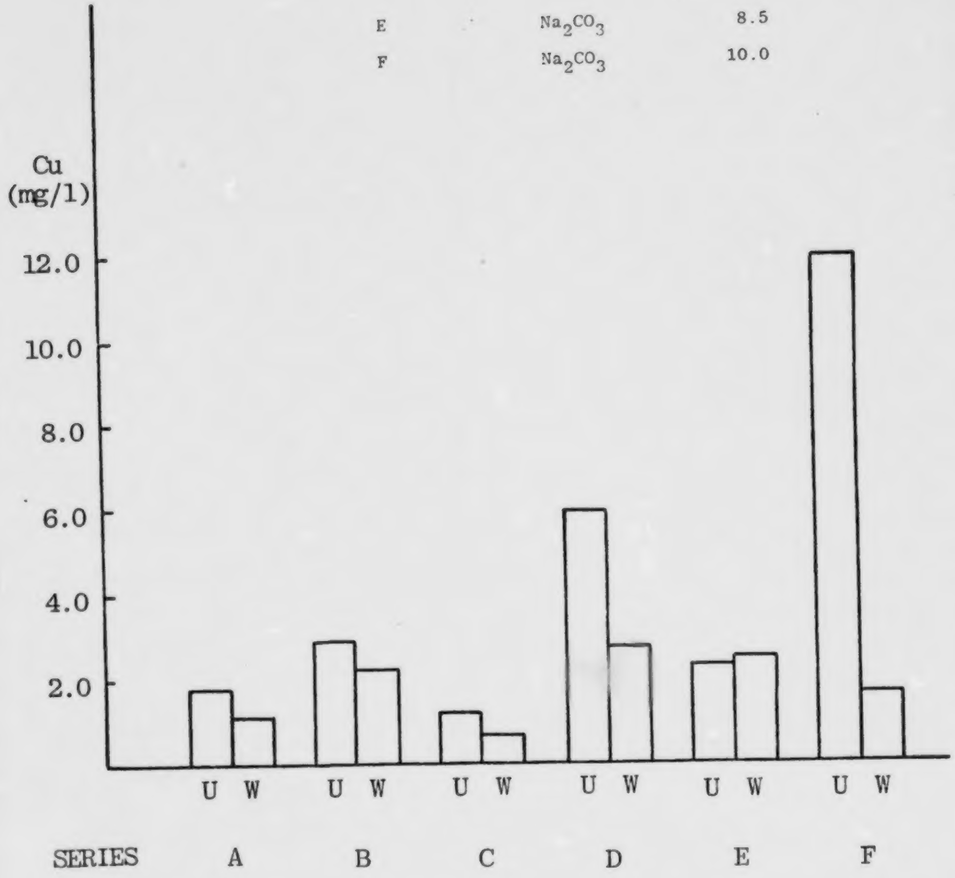
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0



Copper levels in washed (W) and unwashed (U) sludges extracted by the ASTM Method A extraction procedure for plant # 4.

Figure 6-13. Plant #4 Cu in ASTMs-A

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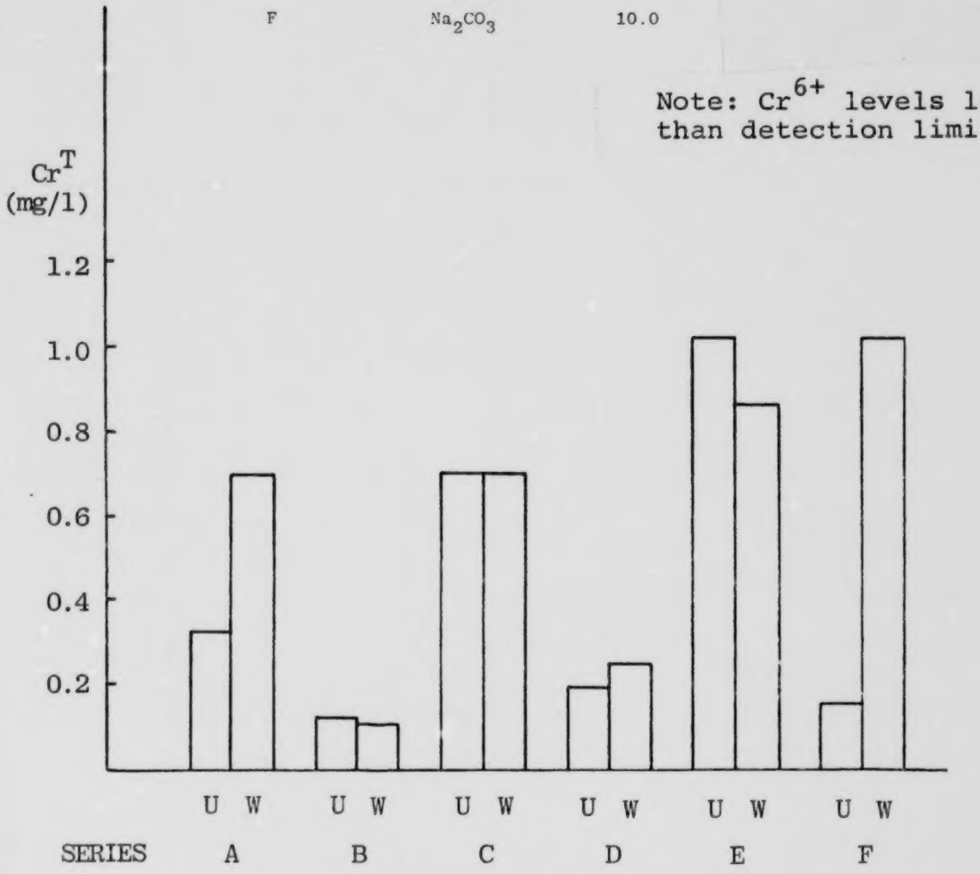
SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Note: Cr^{6+} levels less than detection limit.



Chromium levels in washed (W) and unwashed (U) sludges extracted by the EPA extraction procedure for plant # 4.

Figure 6-14. Plant #4 Cr^T in EPA-EP

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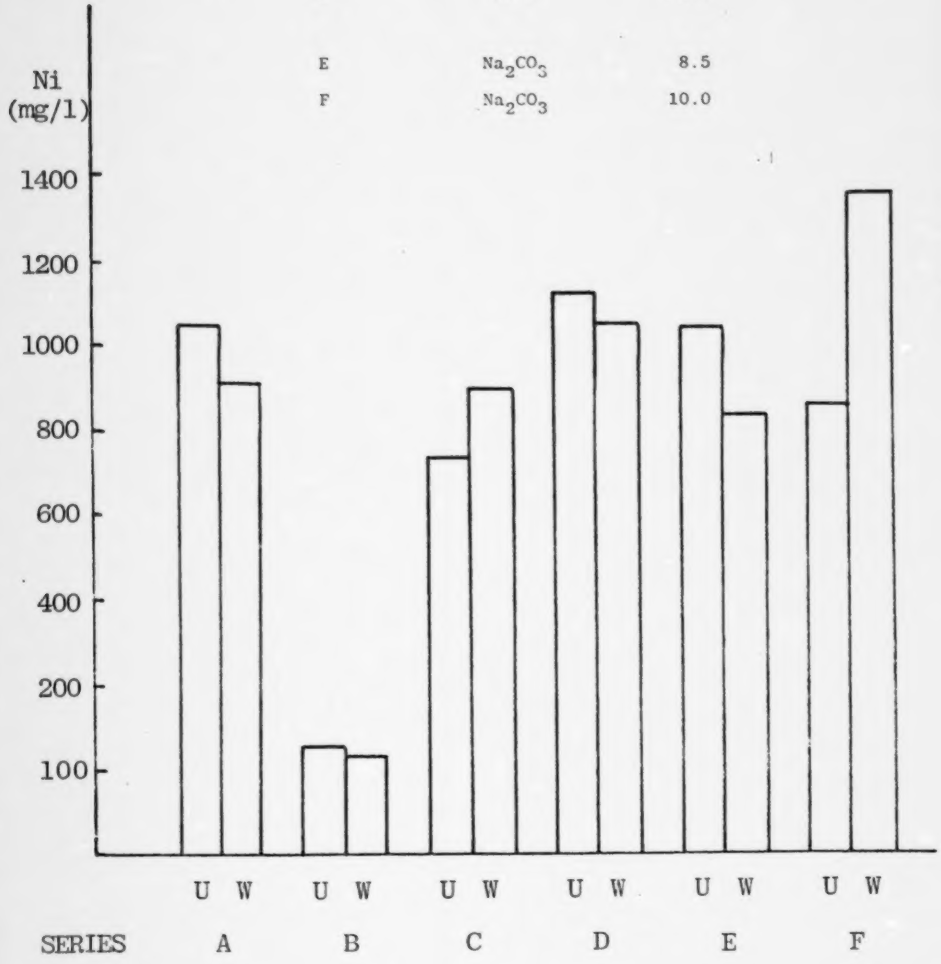
SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0



Nickel levels in washed (W) and unwashed (U) sludges extracted by the EPA extraction procedure for plant # 4.

Figure 6-15. Plant #4 Ni in EPA-EP

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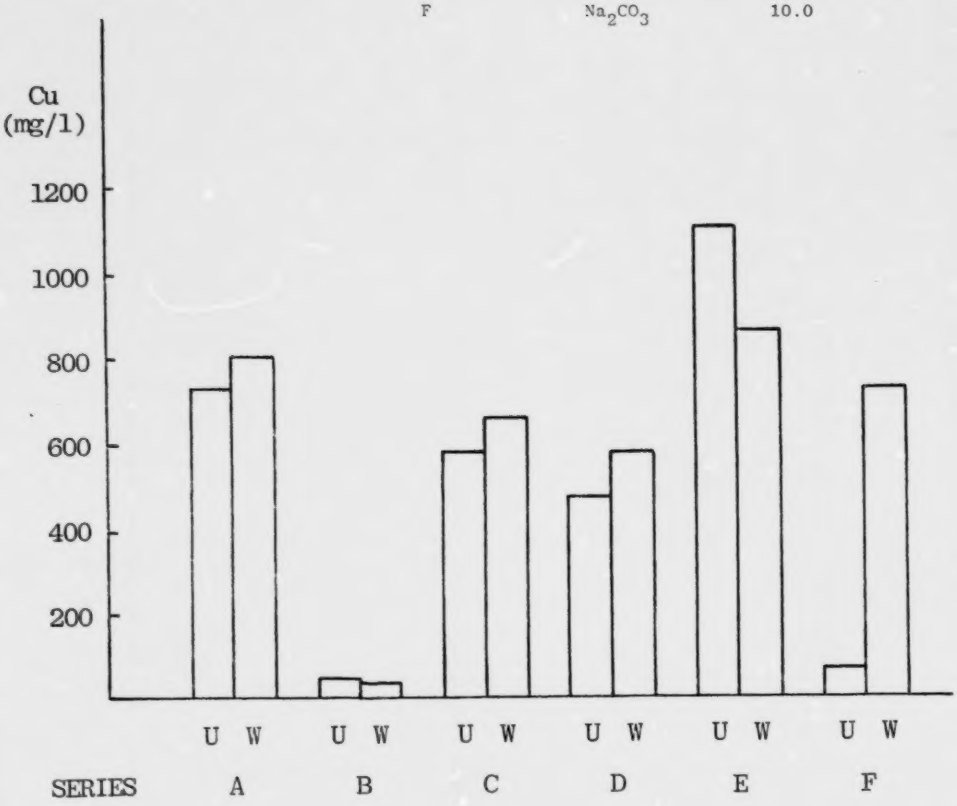
SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0



Copper levels in washed (W) and unwashed (U) sludges extracted by the EPA extraction procedure for plant # 4.

Figure 6-16. Plant #4 Cu in EPA-EP

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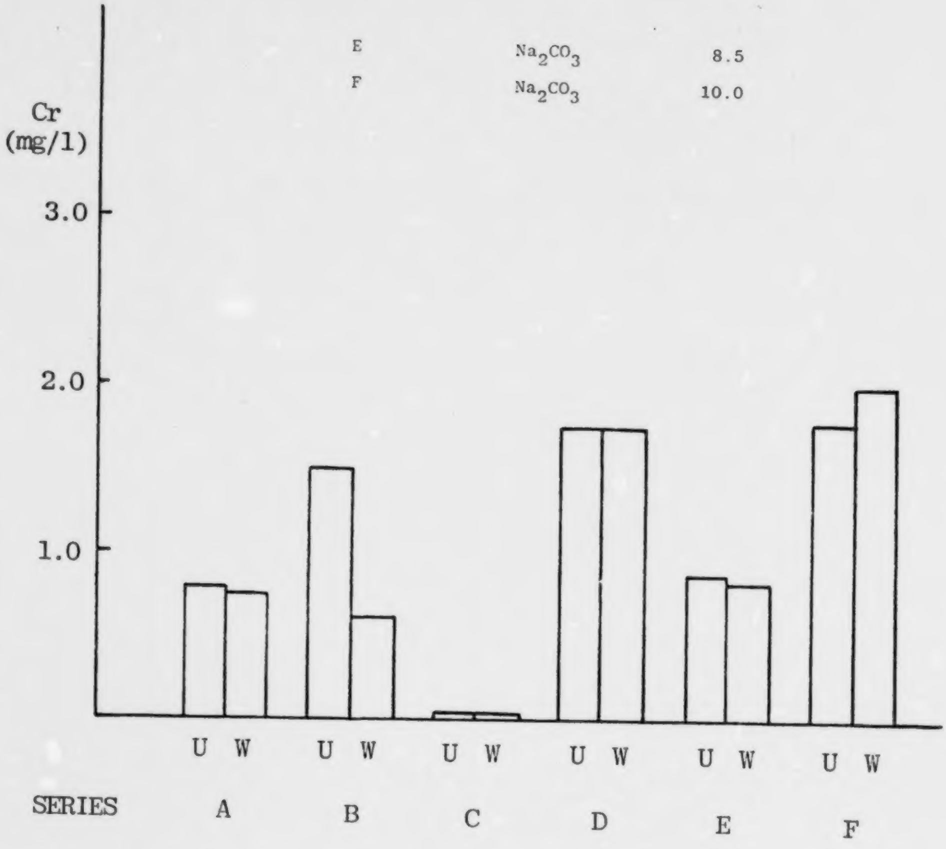
SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0



Chromium levels in washed (W) and unwashed (U) sludges extracted by the ASTM Method A extraction procedure for plant # 6.

Figure 6-17. Plant #6 Cr^T in ASTMs-A

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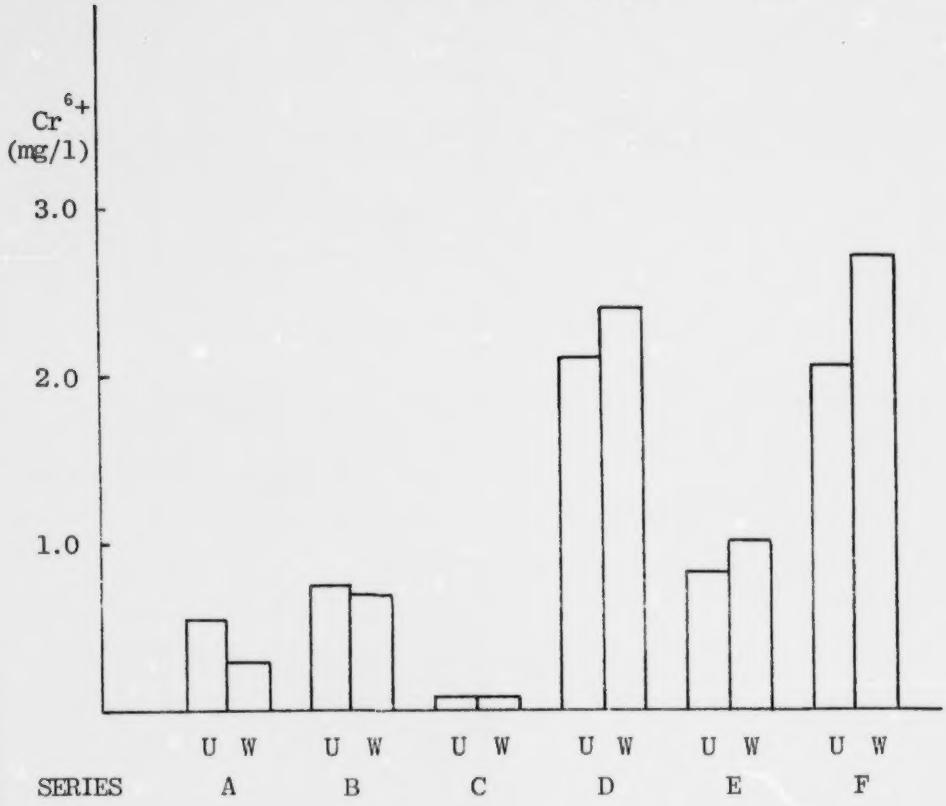
SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0



Hexavalent Chromium levels in washed (W) and unwashed (U) sludges extracted by the ASTM Method A extraction procedure for plant # 6.

Figure 6-18. Plant #6 Cr^{6+} in ASTMs-A

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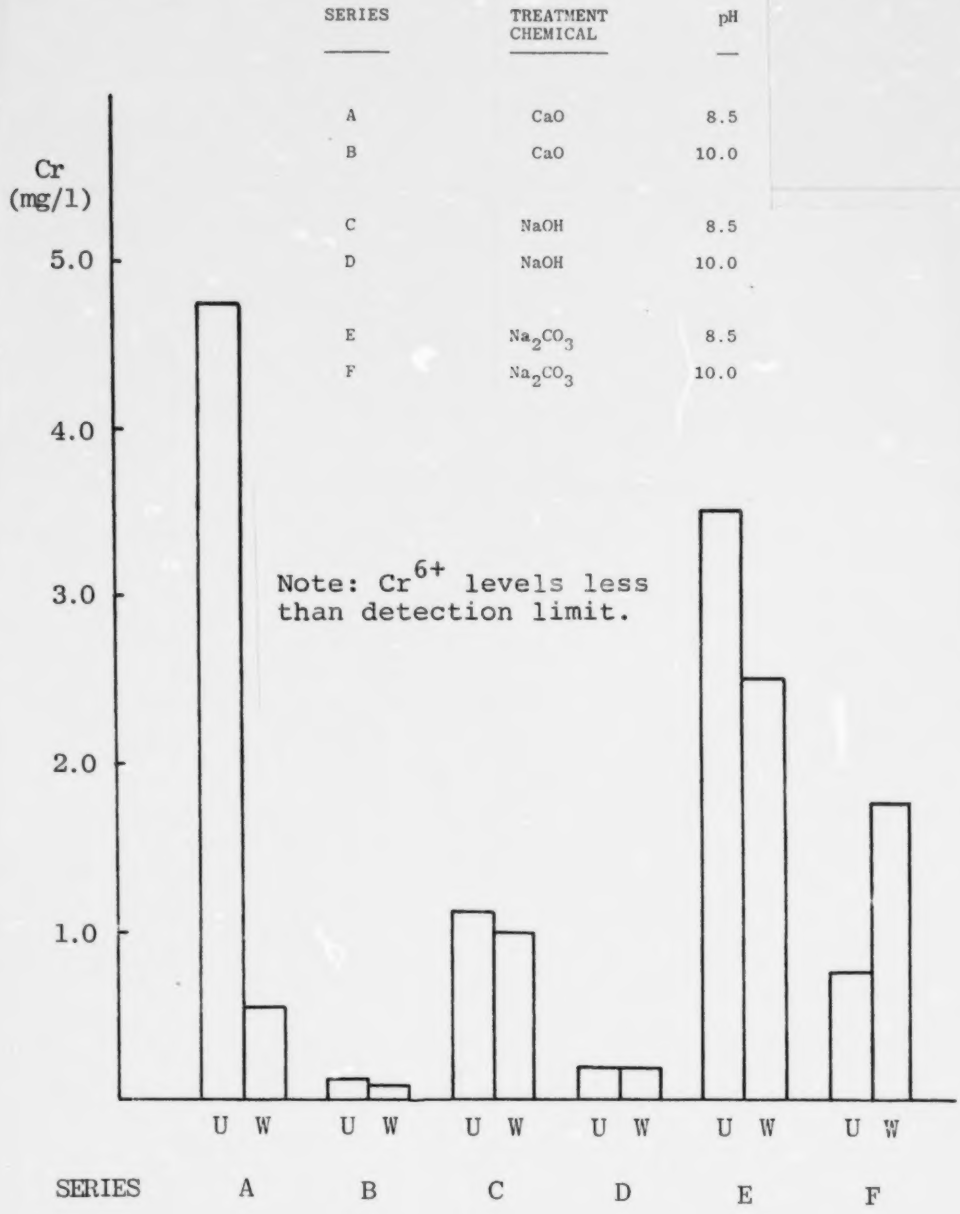

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Note: Cr^{6+} levels less than detection limit.

Chromium levels in washed (W) and unwashed (U) sludges extracted by the EPA extraction procedure for plant # 6.

Figure 6-19. Plant #6 Cr^T in EPA-EP

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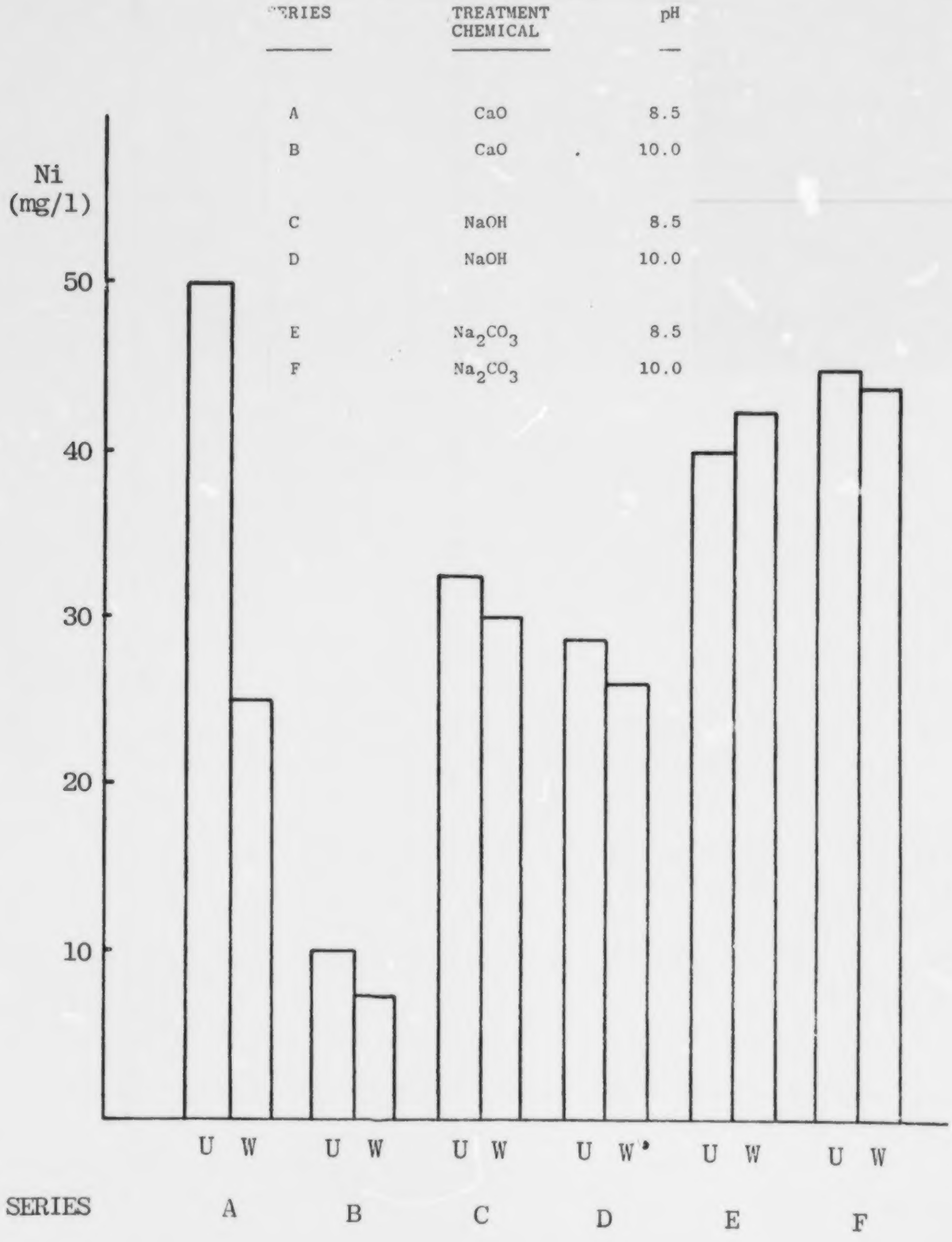

ERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Nickel levels in washed (W) and unwashed (U) sludges extracted by the EPA extraction procedure for plant # 6.

Figure 6-20. Plant #6 Ni in EPA-EP

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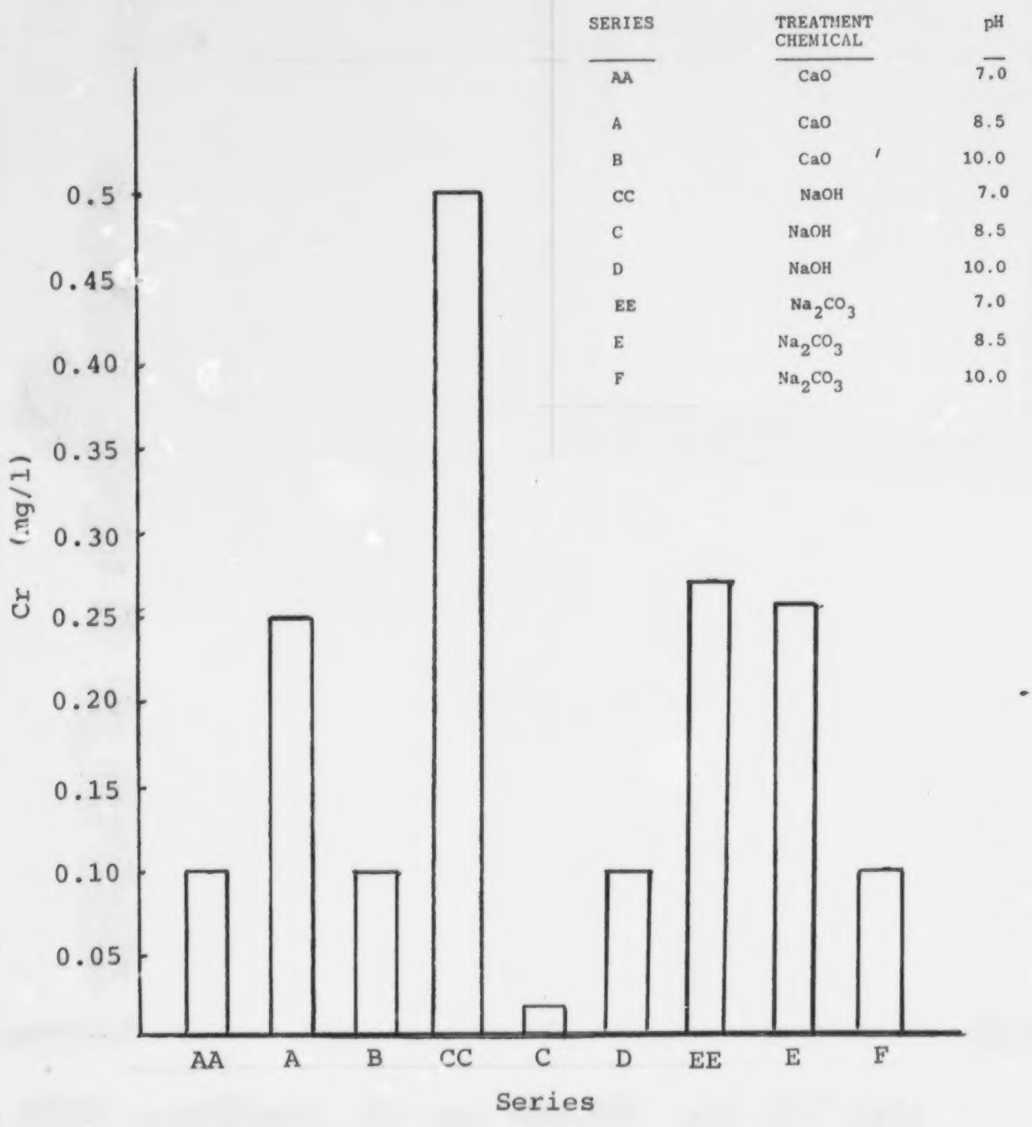

SERIES	TREATMENT CHEMICAL	pH
AA	CaO	7.0
A	CaO	8.5
B	CaO	10.0
CC	NaOH	7.0
C	NaOH	8.5
D	NaOH	10.0
EE	Na_2CO_3	7.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Figure 6-21. Plant #7 Cr^T in ASTMs-A

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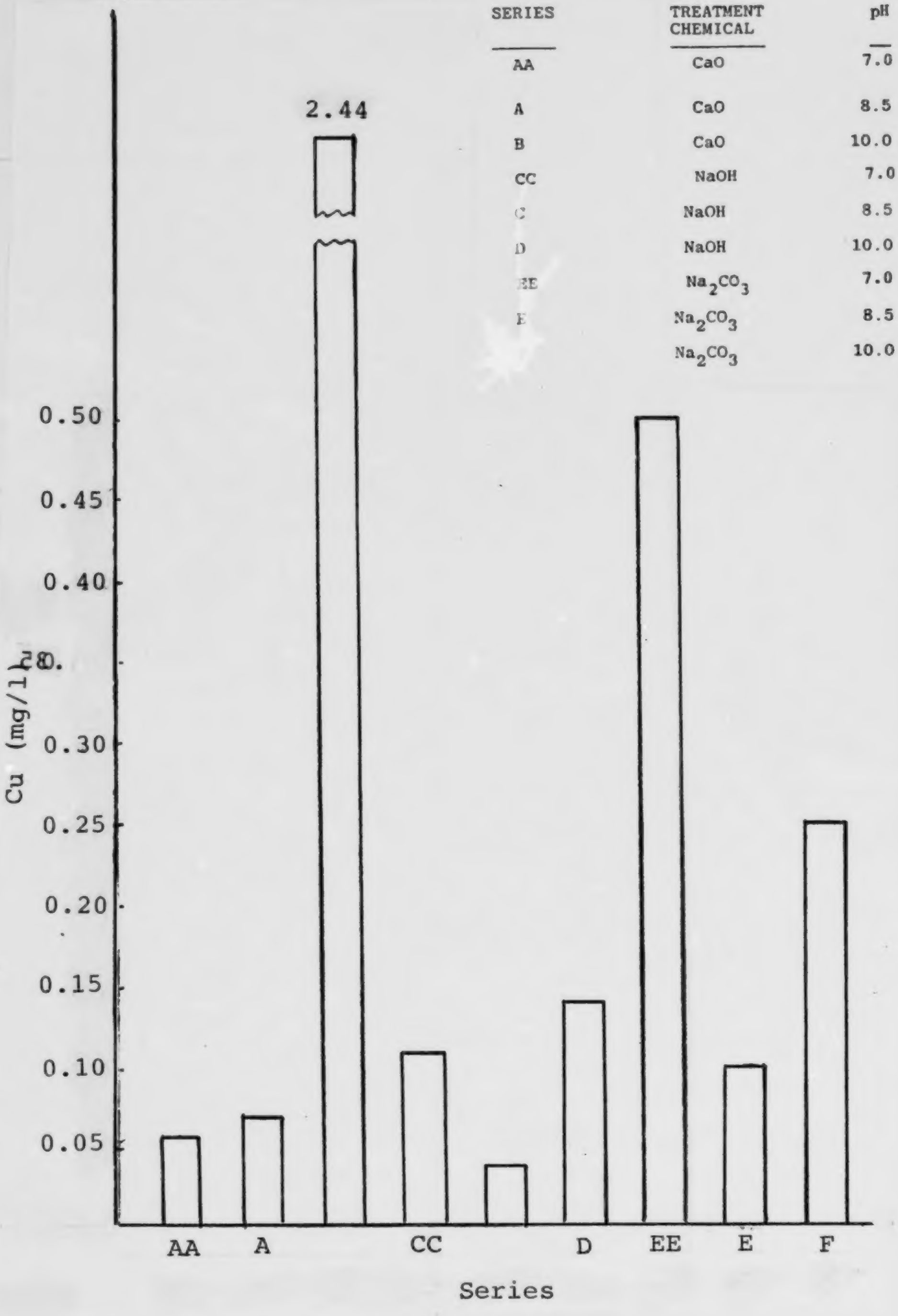

SERIES	TREATMENT CHEMICAL	pH
AA	CaO	7.0
A	CaO	8.5
B	CaO	10.0
CC	NaOH	7.0
C	NaOH	8.5
D	NaOH	10.0
EE	Na_2CO_3	7.0
E	Na_2CO_3	8.5
	Na_2CO_3	10.0

Figure 6-22. Plant #7 Cu in ASTMs-A

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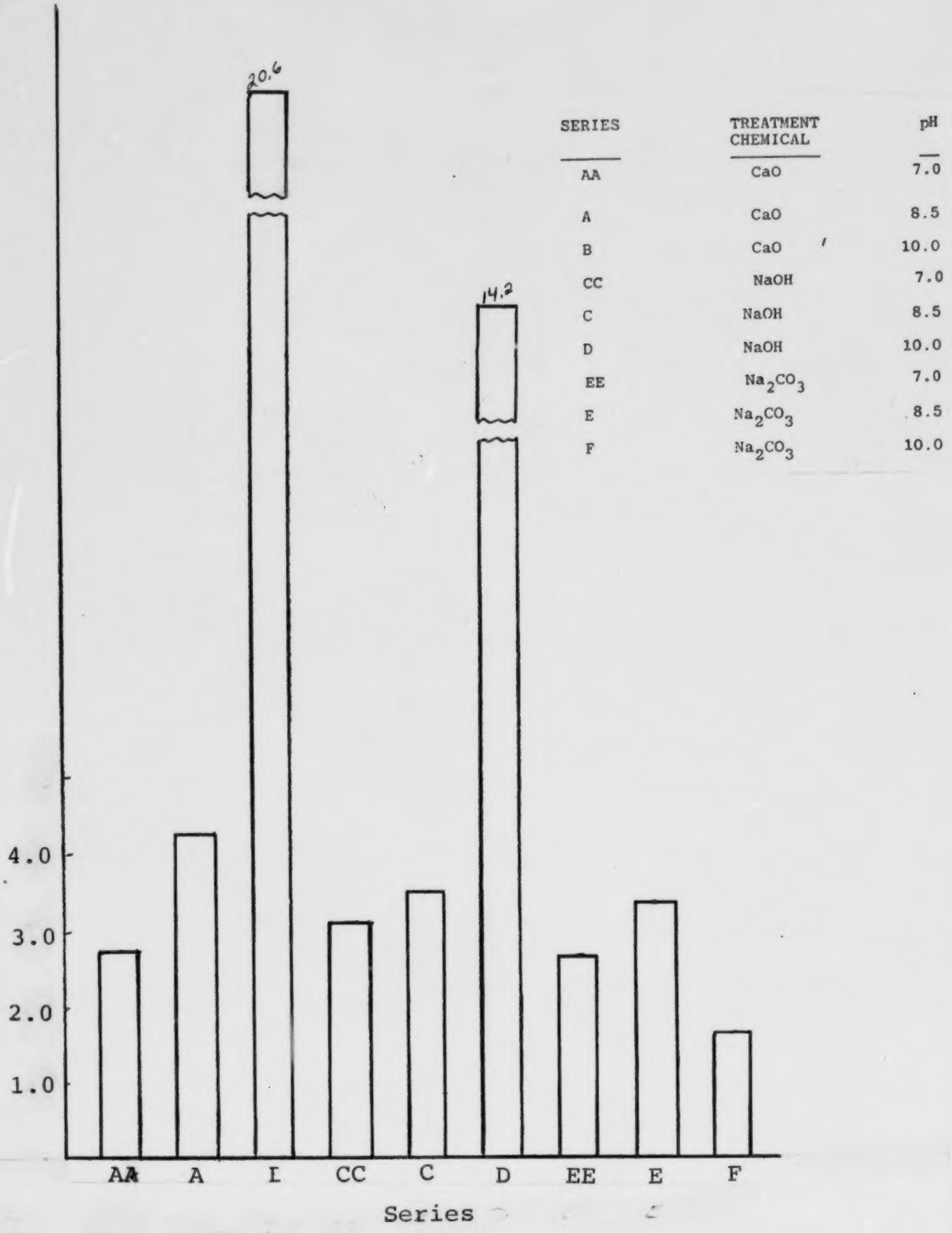

SERIES	TREATMENT CHEMICAL	pH
AA	CaO	7.0
A	CaO	8.5
B	CaO	10.0
CC	NaOH	7.0
C	NaOH	8.5
D	NaOH	10.0
EE	Na_2CO_3	7.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Figure 6-23. Plant #7 Ni in ASTMs-A

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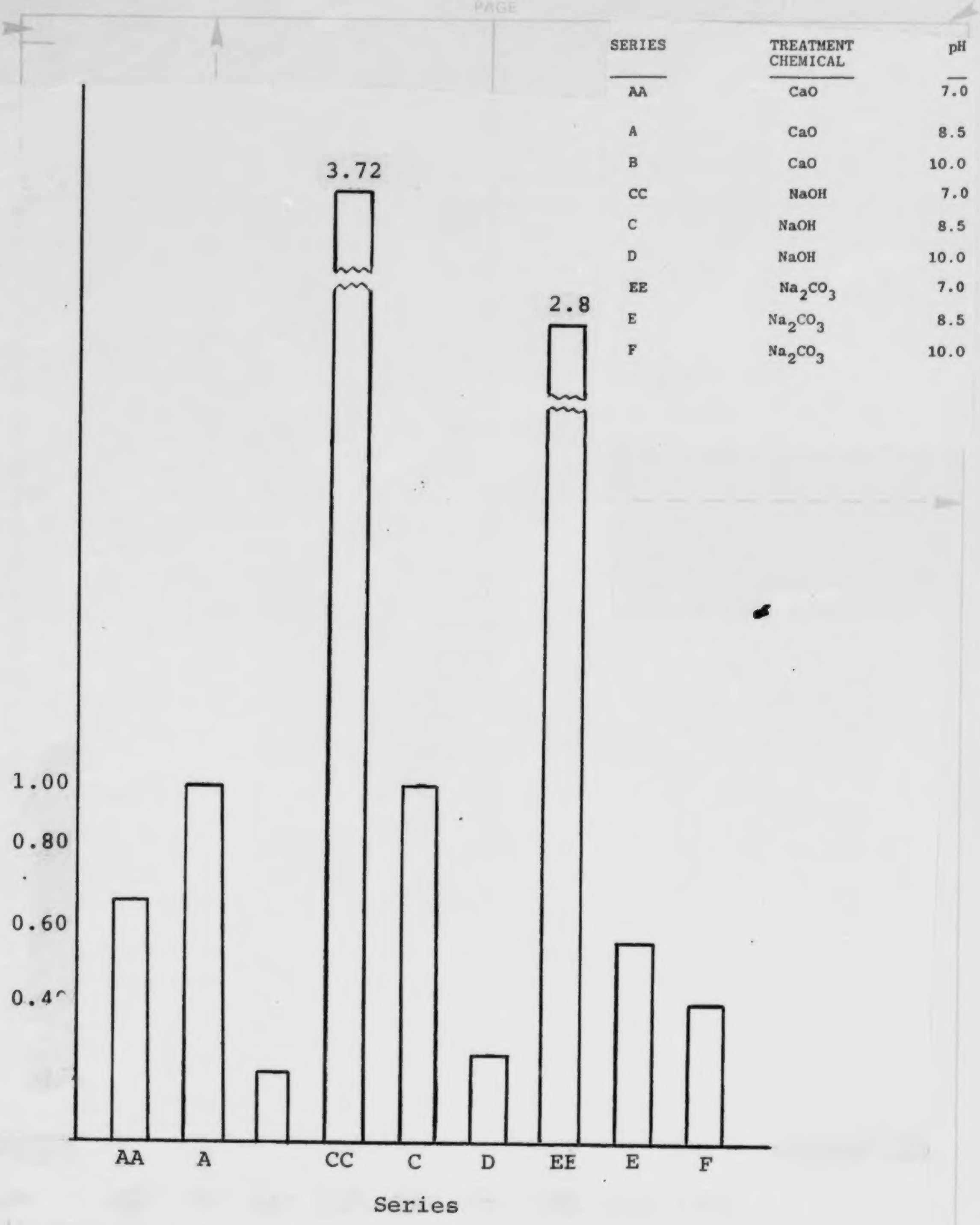


SERIES	TREATMENT CHEMICAL	pH
AA	CaO	7.0
A	CaO	8.5
B	CaO	10.0
CC	NaOH	7.0
C	NaOH	8.5
D	NaOH	10.0
EE	Na_2CO_3	7.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Figure 6-24. Plant #7 Zn in ASTMs-A

what caused this result. The trends through the treatment series for Cr^+ and Cr^{+6} are very similar, tending to corroborate this result.

Plant 8 treatment with Na_2CO_3 produced a floc with very poor settling characteristics. A significant amount of particulate mattter was apparent in the partially cleared supernatant. This sludge cake also was very unstable toward leaching of metals by both ASTM-A, Figures 6-25 through 6-27 and EPA-EP, Figures 6-28 through 6-30 extractions, especially at pH 10. Chromium and copper levels in the EPA-EP extract of Na_2CO_3 precipitated sludges were exceptions and were by contrast the lowest for these metals in the treatment series.

It is apparent from the above that in most cases the metal levels in the ASTM-A extract were lower than in the EPA-EP extract. The pH that produced the least leaching was different for each plant, with some plants' sludges exhibiting similar behavior at both pH's.

The parameters (pH, chemical, or interaction) that showed a statistical significance for a plant, can only be said to be significant for that particular plant. Each of the plants' wastewaters is different and reacts differently under similar circumstances. No generalities seem to apply to sludge leachability, except that the EPA-EP leaches higher levels of metals than the ASTM-A, which was already known before testing began.

Sample Site Identification
(Continued)

Sample Location	ID	Quantity of Sample Taken
Plant 7		
Untreated Acid/Alkali	D1,D2	55-gallons (each)
Treated Cr	D3	55 gallons
Untreated CN	D4,L2	55 gallons, 1 liter
Al Anodizing	D5	55 gallons
Untreated Cr^{+6}	L1	1 liter
Feed to Clarifier	L4	1 liter
Flocculant	L5	1 liter
Clarifier Effluent	L6	1 liter
Treated CN	L7	3 liters
Clarifier Underflow	S1	2.5 gallons
Drying Bed	S2,S3	2.5 gallons (each)
Plant 8		
After Cr Treatment	D1	55 gallons
After Main Sump	D2	55 gallons
After pH Adjust	L1	1 quart
Effluent	L2	1 quart
Filtrate	L3	1 quart
Flocculant (Undiluted)	L4	1 quart
Sludge Pit	S1	2 quarts
Sludge-Dewatered	S2	2 quarts
Clarifier Underflow	S3	2 quarts

fresh water. The rinsewater is therefore continuously circulated and treated.

Spent acid has its own treatment tank. Spent acid is dumped 3 times per week to the treatment tank. Zinc dragout, cadmium dragout and floor spills are all routed to the floor spill tank. When the tanks reach an appropriate level, they are batch treated first to reduce chrome (if their presence is detected by chemical analysis) and then pH adjusted (desired pH = 6.5 to 8).

Solids from the integrated treatment tanks are allowed to settle daily. Every morning the solids are pumped to another settling tank. The solids from the acid and floor spill tanks are pumped, when required, to a different settling tank. Sludge from the two settling tanks is pumped to a sludge tank from which 3,500 gallons of sludge (at 15% solids) are hauled away every three weeks. Effluent from the settling tanks is withdrawn through a filter cloth and discharged to the sewer.

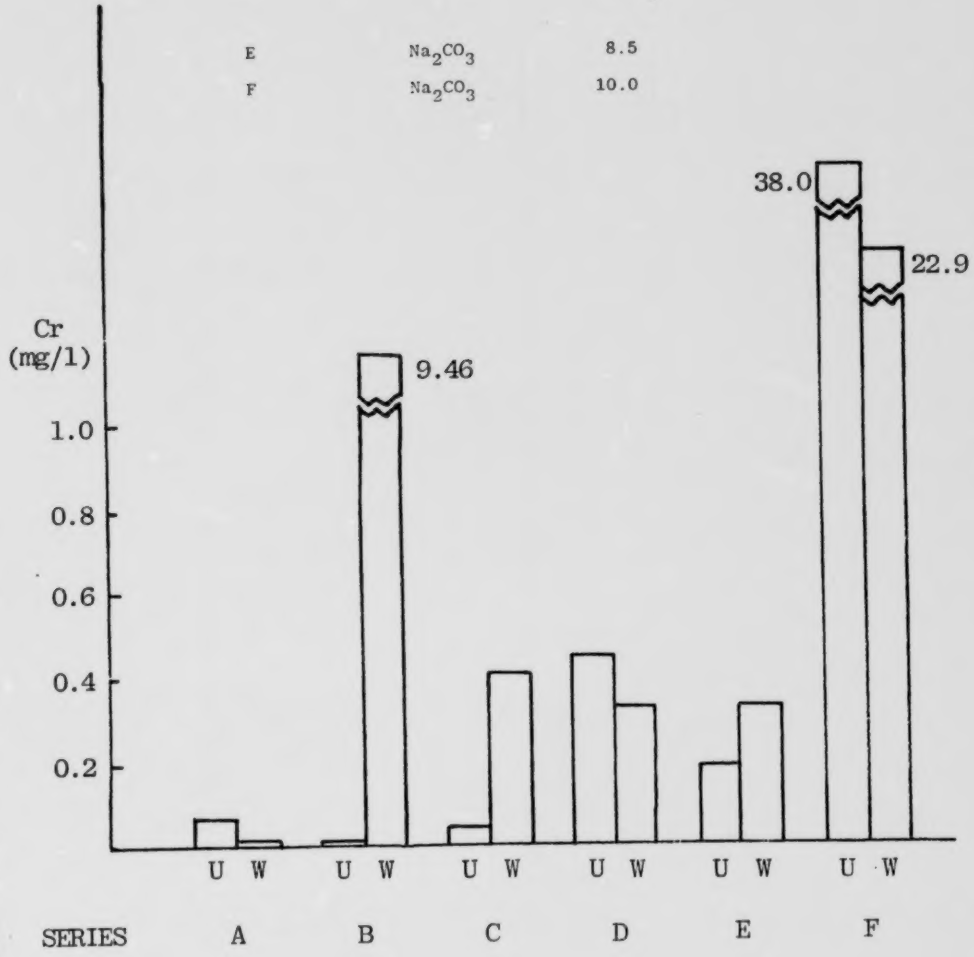
There are four wastewater streams which completely bypass treatment. They are the counter-flow rinse, the cold water rinses following the soap cleaner, zinc rinse, and, following the cadmium line, acid rinse. These streams are discharged to a river and do not receive any downstream treatment.

PLANT #2--SECOND VISIT

Upon arrival at the plant, the wastewater treatment system had been operating for two hours. Due to the nature of the sampling

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Note: Cr^{6+} levels all below detection limit.



Chromium levels in washed (W) and unwashed (U) sludges extracted by the ASTM Method A extraction procedure for plant # 8.

Figure 6-25. Plant #8 Cr^T in ASTMs-A

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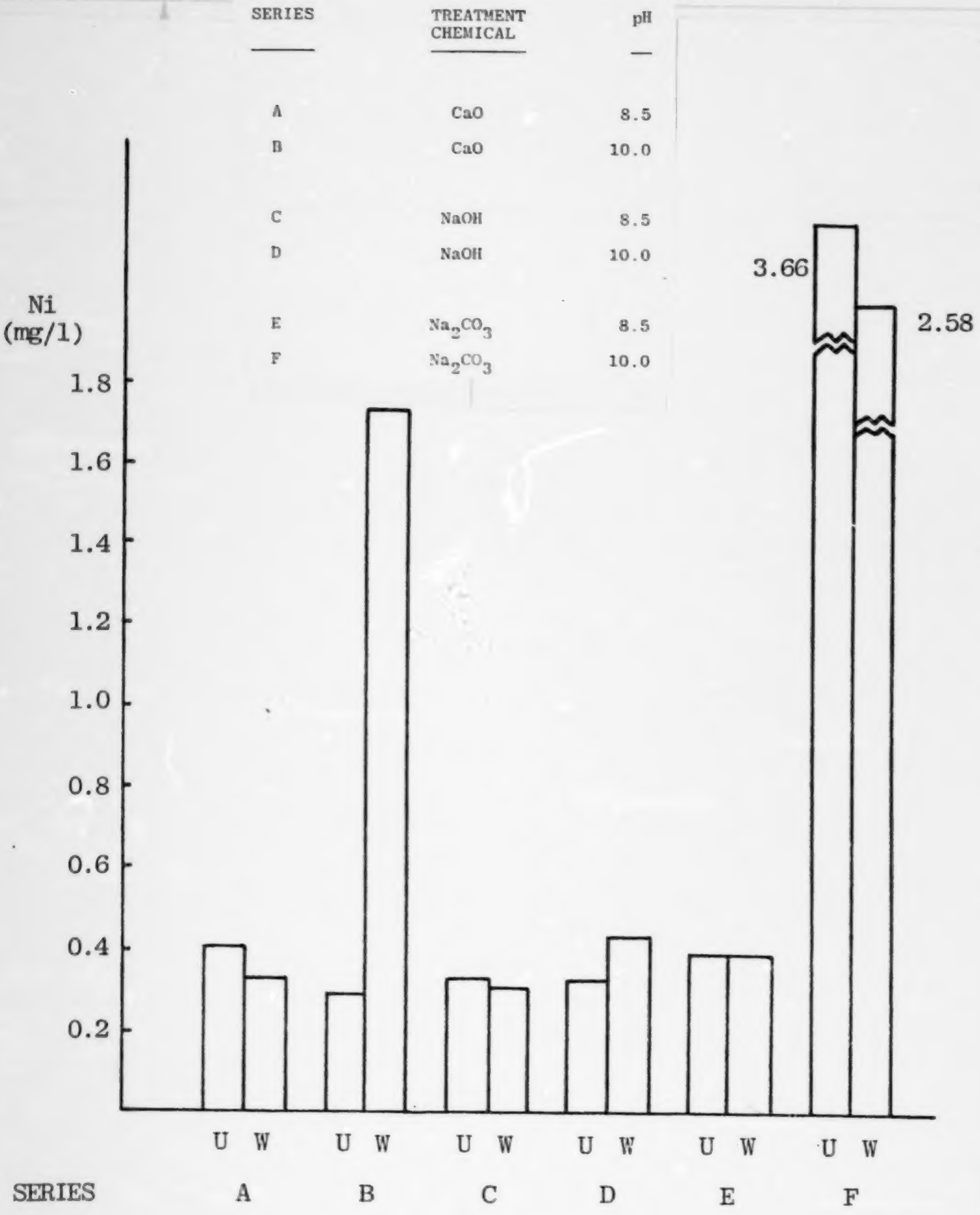
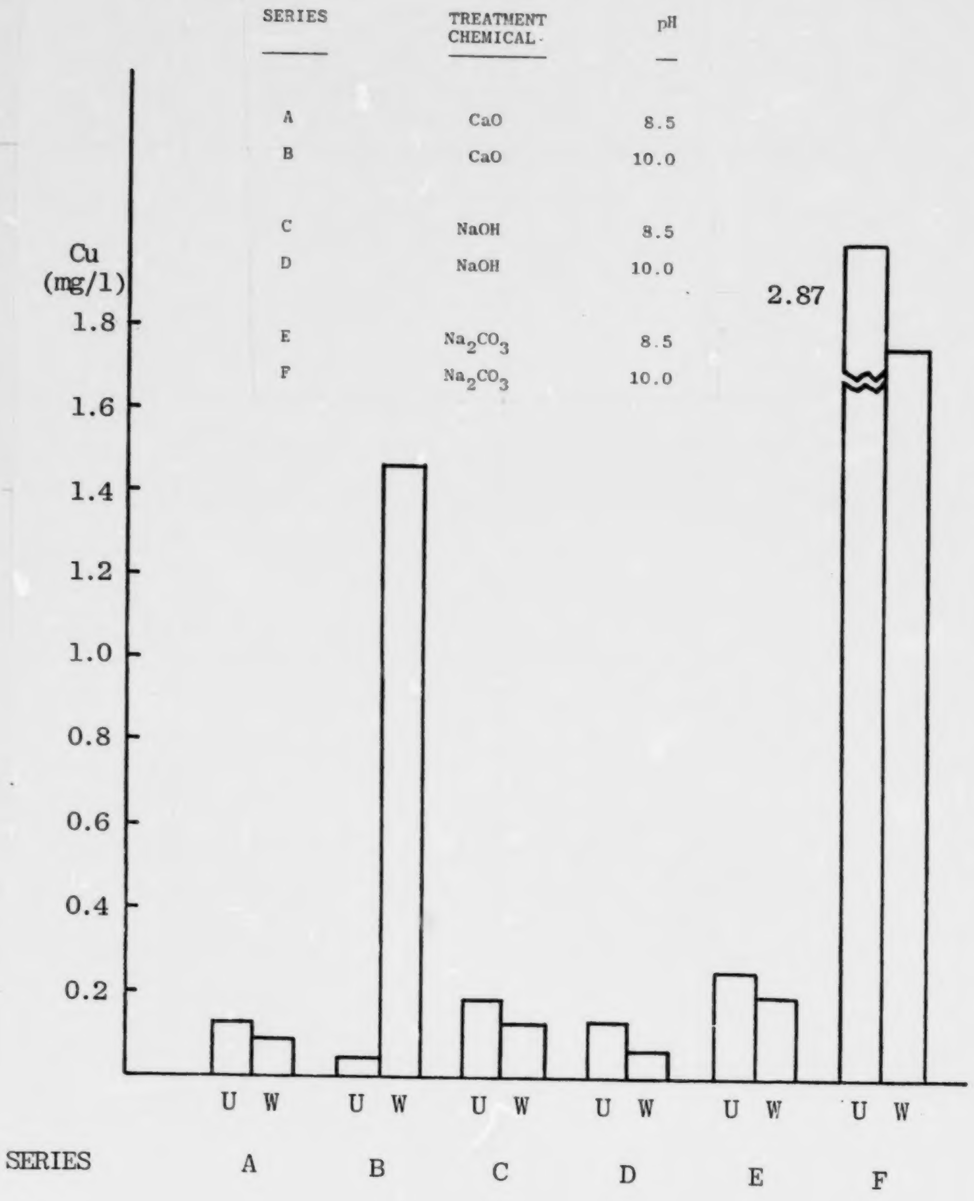


SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Nickel levels in washed (W) and unwashed (U) sludges extracted by the ASTM Method A extraction procedure for plant # 8.

Figure 6-26. Plant #8 Ni in ASTMs-A



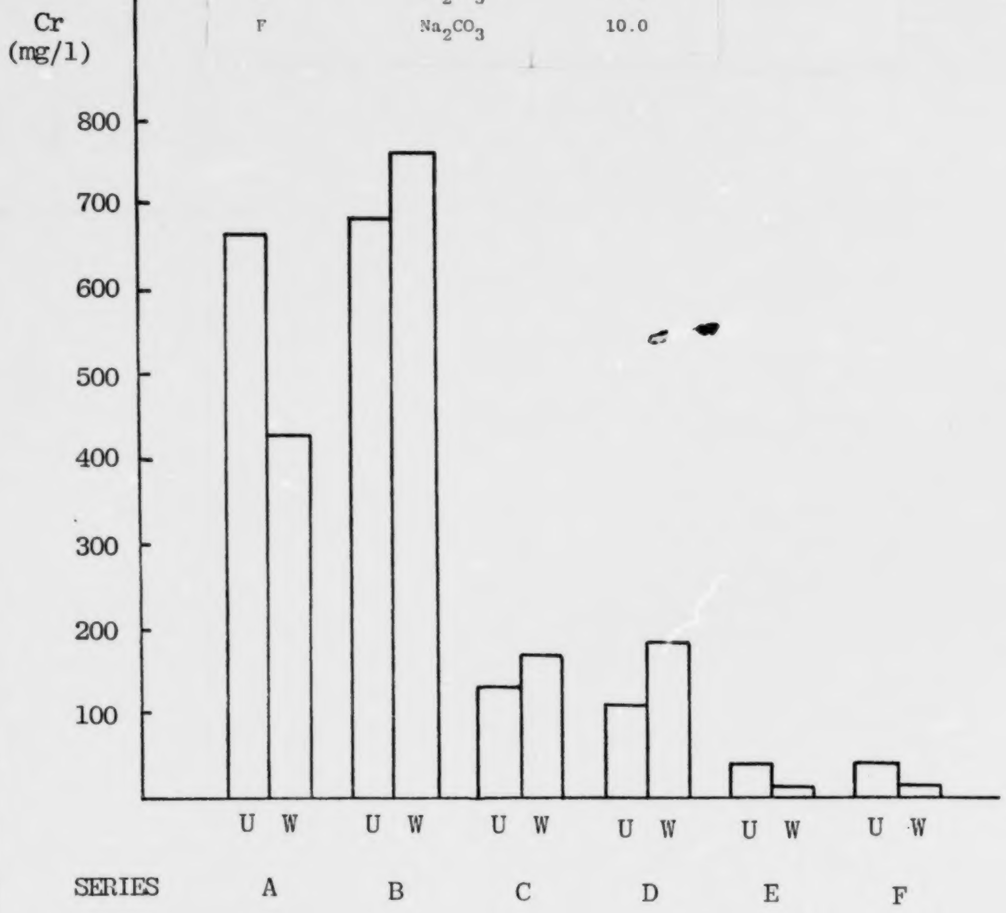
SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Copper levels in washed (W) and unwashed (U) sludges extracted by the ASTM Method A extraction procedure for plant # 8.

Figure 6-27. Plant #8 Cu in ASTMs-A

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Note: Cr^{6+} levels all below detection limit.



Chromium levels in washed (W) and unwashed (U) sludges extracted by the EPA extraction procedure for plant # 8.

Figure 6-28. Plant #8 Cr^T in EPA-EP

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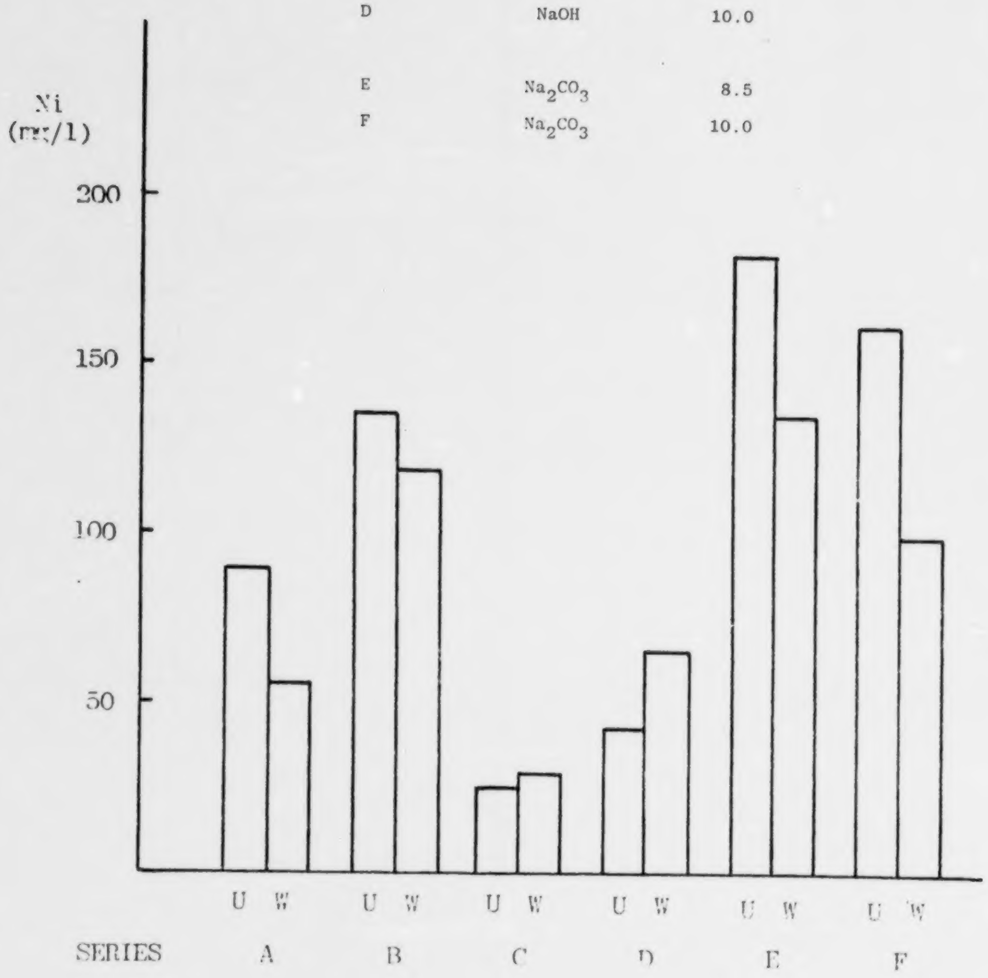
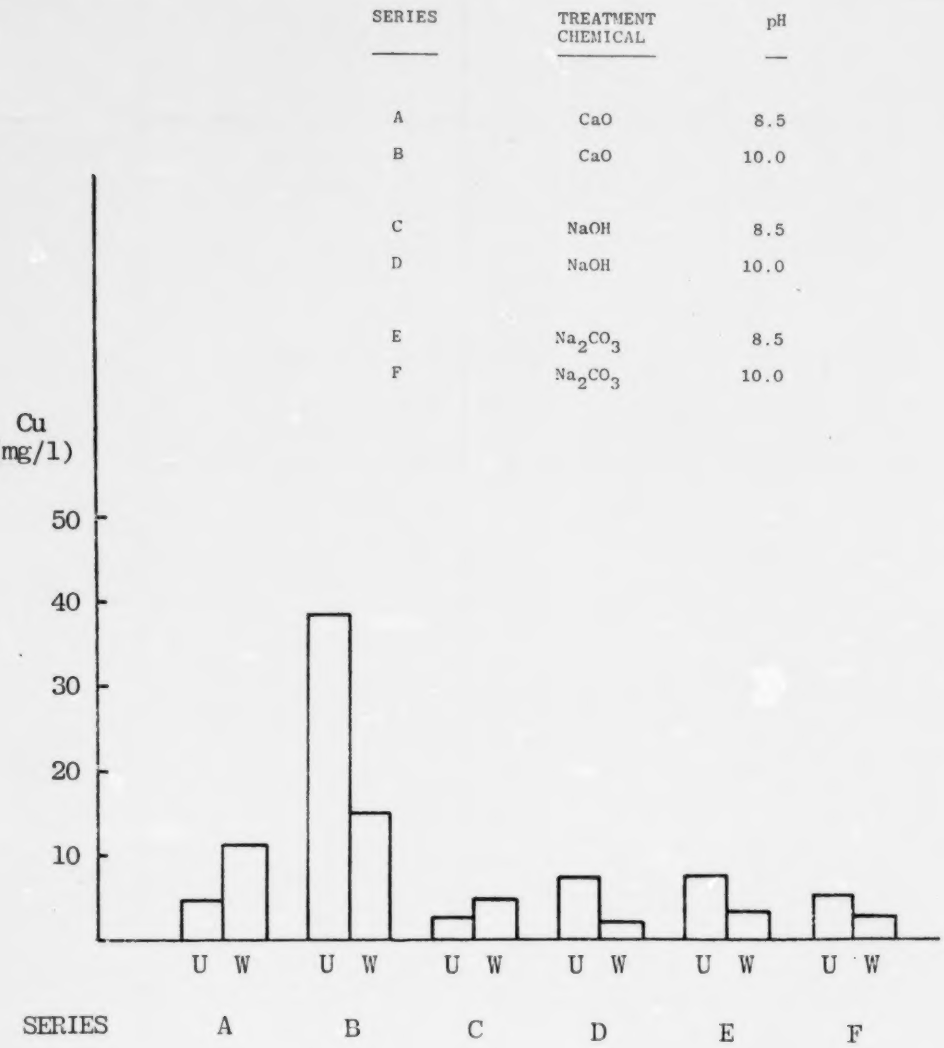
SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0



Nickel levels in washed (W) and unwashed (U) sludges extracted by the EPA extraction procedure for plant # 8.

Figure 6-29. Plant #8 Ni in EPA-EP



SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Copper levels in washed (W) and unwashed (U) sludges extracted by the EPA extraction procedure for plant # 8.

Figure 6-30. Plant #8 Cu in EPA-EP

6.4 ANALYSIS OF EFFECTS ON SLUDGE DEWATERABILITY

During the filter-leaf tests, fresh sludge dewatered fastest for Plants 2, 4 and 6, while aged sludge dewatered fastest for Plants 3 and 8. The fresh sludges that proved best were from different chemical treatments, but all were at pH 8.5. The best aged sludges were found at both pH 8.5 and 10. A pH of 8.5 in conjunction with any of the three treatment chemicals produced sludges from Plants 4 and 6 that dewatered better than the same sludge at pH 10. This comparison is for fresh sludge at pH 8.5 versus fresh sludge at pH 10, and similarly for aged sludge.

It was found that in most cases fresh sludge filtered faster than aged sludge, though not exclusively. As with other testing parameters, each plant's sludge behaved differently.

Apparently, both the precipitation chemical and precipitation pH have little effect on sludge dewatering by vacuum filtration.

6.5 POTENTIAL FOR QUICK ACCEPTANCE TEST

An analysis was performed to demonstrate the potential for a quick acceptance test based on metal levels in any of the waters associated with the plant sludges. Metal levels in the effluent, interstitial, and wash waters were correlated with their respective metal levels in the EPA-EP and ASTM-A extract.

Initially, simple correlations were performed for each metal at each plant. Results are presented in Section 10. None of the waters associated with the sludge appear to show any promise of being related to the EPA-EP results in a manner that could lead to broad application. Even in those few cases where a high correlation is seen for a particular plant, the relation is found to be in the opposite direction for another plant.

However, in the case of the ASTM-A extract results, Appendix IV shows that the sludge filtrate analysis (washed or unwashed) displays a positive correlation for most metals at most plants. Therefore, the results of the sludge filtrate analyses (unwashed) were correlated with the ASTM-A extract results for each metal for all plants taken together. Results are shown in Table 6-5.

Table 6-5 shows that the correlation derived for each metal is significant. The sample correlation coefficient r is given followed by the sample size. The 95 percent confidence limits on the population correlation coefficient are also given. Since in no case do these limits include zero (no correlation), it can be stated with a high degree of confidence that the metal content of the sludge filtrate does correlate with the results of the ASTM-A extraction. This fact does indicate that there is potential for development of a quick acceptance test for operators of segregated nonhazardous waste landfills. Additional data and analysis to determine the fit of various regression models are needed to confirm this potential and to derive the desired quick acceptance test methodology.

Table 6-5

Correlation of Filtrate (Unwashed) with ASTM-A Results

Metal	Sample Correlation Coefficient, r	No. of Data Points	95 Percent Confidence Limits
Cd	.942	12	$.78 < \rho < .99$
Cr	.638	30	$.35 < \rho < .81$
Cu	.936	12	$.59 < \rho < .95$
Ni	.936	18	$.81 < \rho < .98$
Zn	.970	6	$.67 < \rho < .99$

SECTION 7

PLANT TRIP REPORTS

PLANT # 2--FIRST VISIT

This plant plates acid zinc and acid cadmium onto metal screws. One barrel line is present in the plant and serves both plating tanks. Plant operation is normally 12 hours per day, 5 days per week. Currently the plant is operating 18-20 hours per day, Monday through Friday, and 6 hours on Saturday. Water saving techniques such as counter-flow rinsing and water savers are in use.

The wastewater treatment system operates on the same cycle as the plating shop and is composed of large continuous treatment tanks. Acid, cadmium, chromate, and zinc waste streams are processed in integrated treatment tanks. The four integrated treatment systems are similar except for specific reagents and pH control points. Zinc treatment will be used for the discussion. The first rinse tank after zinc plating continuously overflows to the zinc sump where the rinsewater is transferred to the zinc loop treatment tank. In this tank, caustic and soda ash are added by the pH controller. A sidestream from the zinc treatment tank is pumped back to the zinc rinse tank in place of

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Sample Location	ID	Quantity of Sample Taken
Plant 2		
Yellow Chrome Bath	1	3 quarts
Zinc Plating Bath	2	3 quarts
Cadmium Plating Bath	3	3 quarts
Acid Pickle Bath	4	3 quarts
Plant Effluent	5	1 quart
Zn Dragout	6	3 quarts (not able to collect)
Cd Dragout	7	3 quarts (not able to collect)
Spent Acid	8	2 quarts
Blue Chromate Bath	9	3 quarts
Plant 3		
Acid Sump (Barrel)	D1	1 drum
Acid Sump (Rack)	D2	1 drum
After CN Oxidation	D3	1 drum
Clear Cr (Treated)	L1	1 liter
Yellor Cr (Treated)	L2	1 liter
CdCN Rinse	L3	2 liters
Other CN Rinse	L4	2 liters
Acid Rinse (Barrel)	L5	1 liter
After CN Oxidation	L6	1 liter
After pH Adjust	L7	1 liter
Effluent	L8	1 liter
Centrate	L9	1 liter
$FeSO_4$	L10	2 liters
Underflow	S1	0.5 gallon
Sludge	S2	0.5 gallon

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Sample Site Identification
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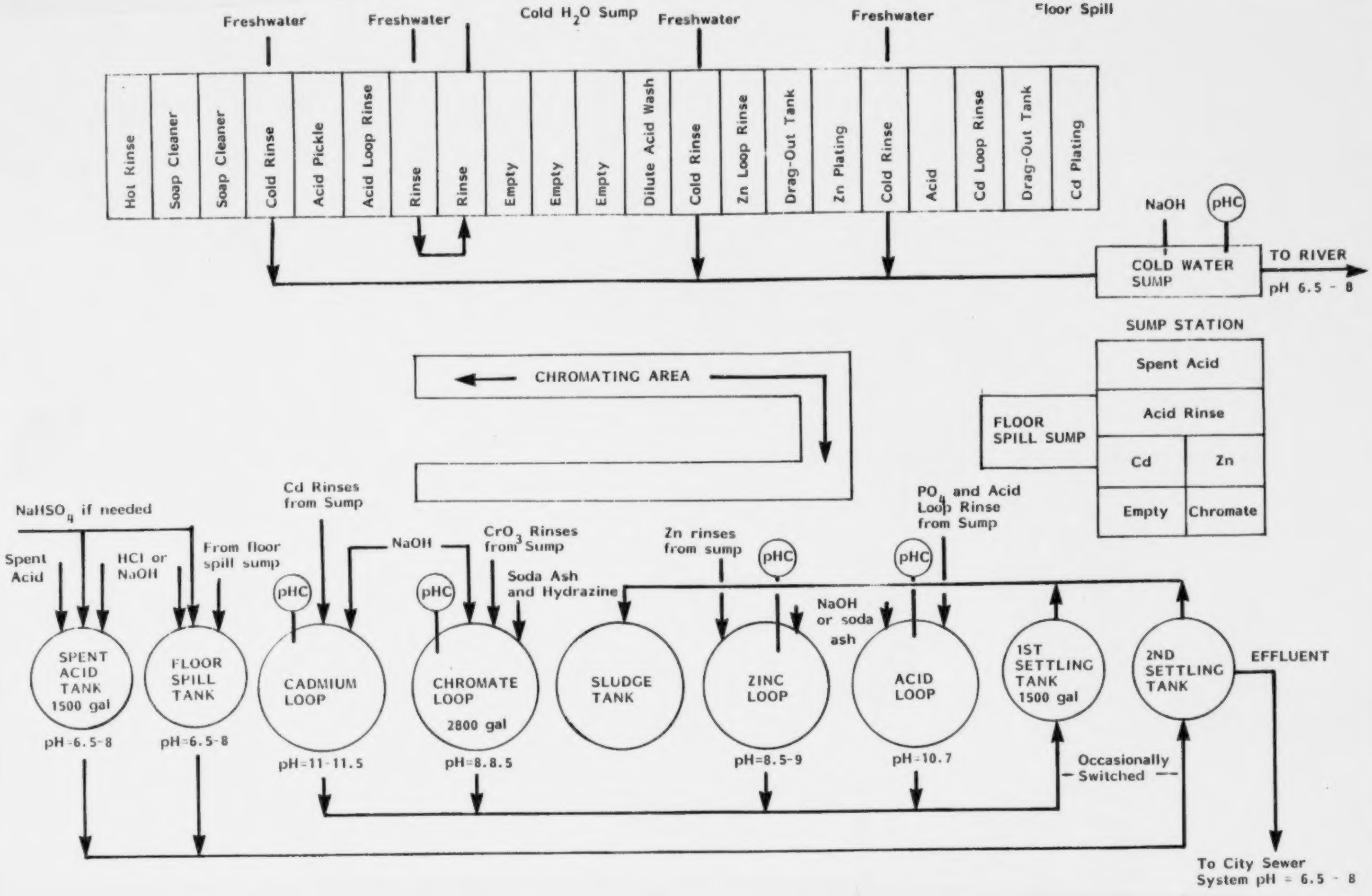
Sample Location	ID	Quantity of Sample Taken
Plant 4		
Treated Cyanide Rinse Water	D1	55 gallons
Nickel Rinse Water	D2	55 gallons
Cleaner Rinse Water	D3	55 gallons
Treated Cyanide Rinse Water	L1	1 quart
Combined Effluent Before Settling	L2	1 quart
Effluent to Pond	L3	1 quart
Filtrate from Filter Press	L4	1 quart
Undiluted Flocculant	L5	1 quart
Prepared Flocculant Solution	L6	1 quart
Sludge from Pit	S1	2 quarts
Filter Cake from Filter Press	S2	2 quarts
Plant 6		
After Chrome Reduction	D1	1 quart
Combined Acid Rinses	D2	55 gallons
After Mix Tank	D3	55 gallons
Flocculant	L1	1 quart
After Mixing Tank	L2	1 quart
Clarifier Overflow	L3	1 quart
Final Effluent to River	L4	1 quart
Filtrate from Belt Filter	L5	1 quart (not able to collect)
Sludge from Clarifier	S1	2 quarts
Sludge from Thickener	S2	2 quarts (not able to collect)
Filter Cake	S3	2 quarts


Freshwater
Freshwater
Cold H₂O Sump
Freshwater
Freshwater
Floor Spill
Hot Rinse
Soap Cleaner
Soap Cleaner
Cold Rinse
Acid Pickle
Acid Loop Rinse
Rinse
Rinse
Empty
Empty
Empty
Dilute Acid Wash
Cold Rinse
Zn Loop Rinse
Drag-Out Tank
Zn Plating
Cold Rinse
Acid
Cd Loop Rinse
Drag-Out Tank
Cd Plating
NaOH
pHC
COLD WATER SUMP
TO RIVER
pH 6.5 - 8
SUMP STATION
Spent Acid
Acid Rinse
Cd
Zn
Empty
Chromate
FLOOR SPILL SUMP
CHROMATING AREA
NaHSO₄ if needed
Spent Acid
HCl or NaOH
From floor spill sump
Cd Rinses from Sump
NaOH
CrO₃ Rinses from Sump
Soda Ash and Hydrazine
Zn rinses from sump
NaOH or soda ash
PO₄ and Acid Loop Rinse from Sump
pHC
pHC
pHC
pHC
SPENT ACID TANK 1500 gal
FLOOR SPILL TANK
CADMIUM LOOP
CHROMATE LOOP 2800 gal
SLUDGE TANK
ZINC LOOP
ACID LOOP
1ST SETTLING TANK 1500 gal
2ND SETTLING TANK
EFFLUENT
pH=6.5-8
pH=6.5-8
pH=11-11.5
pH=8.8.5
pH=8.5-9
pH=10.7
Occasionally Switched
To City Sewer System pH = 6.5 - 8

Plant #2 - Wastewater Treatment System for Chromate Dips and Plating Acid Zinc and Acid Chromium at this plant, it was not necessary to wait longer before sampling. There were no spills or dumps during the time we were sampling. All samples were grab samples. Sample containers were air freighted to the laboratory.

Rinse water flows that were not controlled by flow limiting orifices were determined by displacement tests and by weir calculations. On the attached diagram are shown the wastewater flow rates, tank volumes and retention times.

The plant uses 11 rinses including still, overflow, closed-loop and cascading rinse tanks. Flow restrictors were used on the overflow rinses and the cascading rinse. The closed-loop rinsewater is continuously treated and returned to the rinse tank. The flow rate of the acid loop was calculatd to be 12.33 gpm from displacement measurements. The zinc loop rinsewater flow was calculated to be 15 gpm from measurements of the overflow weir. Cadmium plating was not operating but due to the similarity of equipment with the zinc line, we can assume the cadmium loop rinsewater flows at 15 gpm.

Spent acid, zinc loop, cadmium loop, and acid loop are treated with sodium hydroxide in their own treatment tanks. The acid loop, however, was over-treated during our sampling. The chromate loop is treated with caustic, soda ash and hydrazine to reduce and precipitate chrome.

Residence times for the cadmium and zinc loop treatment tanks are approximately 3 hours. The acid loop tank residence tme is 3.78 hours, and the chromate loop tank residence time is 9.33 hours. Spent acid is accumulated and treated in batches so residence time varies. All dumps and spills are routed to the floor spill sump. The floor spill tank is treated as required for pH adjustment and chrome reduction. The treatment system had been operating 16 hours per day, 5 days per week.

PLANT 3A AND 3B

Plant #3 consists of two job shops which have been designated A and B. Plant 3A plates copper and zinc while 3B can solder dip and plate copper and cadmium. Both shops use chromate dips and each generates approximately 170 gpm of wastewater.

Plant 3A operates 18 hours per day, 5 days per week with the majority of work being performed during the first nine hours. The shop uses water saving techniques such as counter-current rinsing, water savers, and turning rinses off when not in use. The waste treatment facility operates 24 hours per day. Cyanide wastes are collected in a sump from which they are pumped to a three-stage reactor. In the first stage, cyanide is treated with sodium hypochlorite. After cyanide oxidation, the wastewater overflows into a pH adjustment tank. Spent hydrochloric acid is hauled away for disposal while other acidic wastes and rinses are routed to a collection sump. From the sump, the wastewater is transferred to the same pH adjustment tank as the treated cyanide waste. Wastewaters are treated with caustic to obtain a pH of 9-9.5. The overflow from the pH tank enters a 10,000 gallon clarifier. Effluent from the clarifier goes to the sewer for final treatment by the MSD. Sludge from the clarifier goes to a bowl centrifuge for further dewatering. The centrate is recycled to the acid sump while the solids, at 15%, are stored in drums until disposed. Approximately 2,000 gallons/month of sludge (diluted to 12% solids for pumping) are hauled away by tank truck to a landfill. Hauling presently costs 21¢/gallon. Caustic used at the plant is made up from sodium hydroxide beads. Sodium hypochlorite solution is purchased in 1,000 gallon loads.

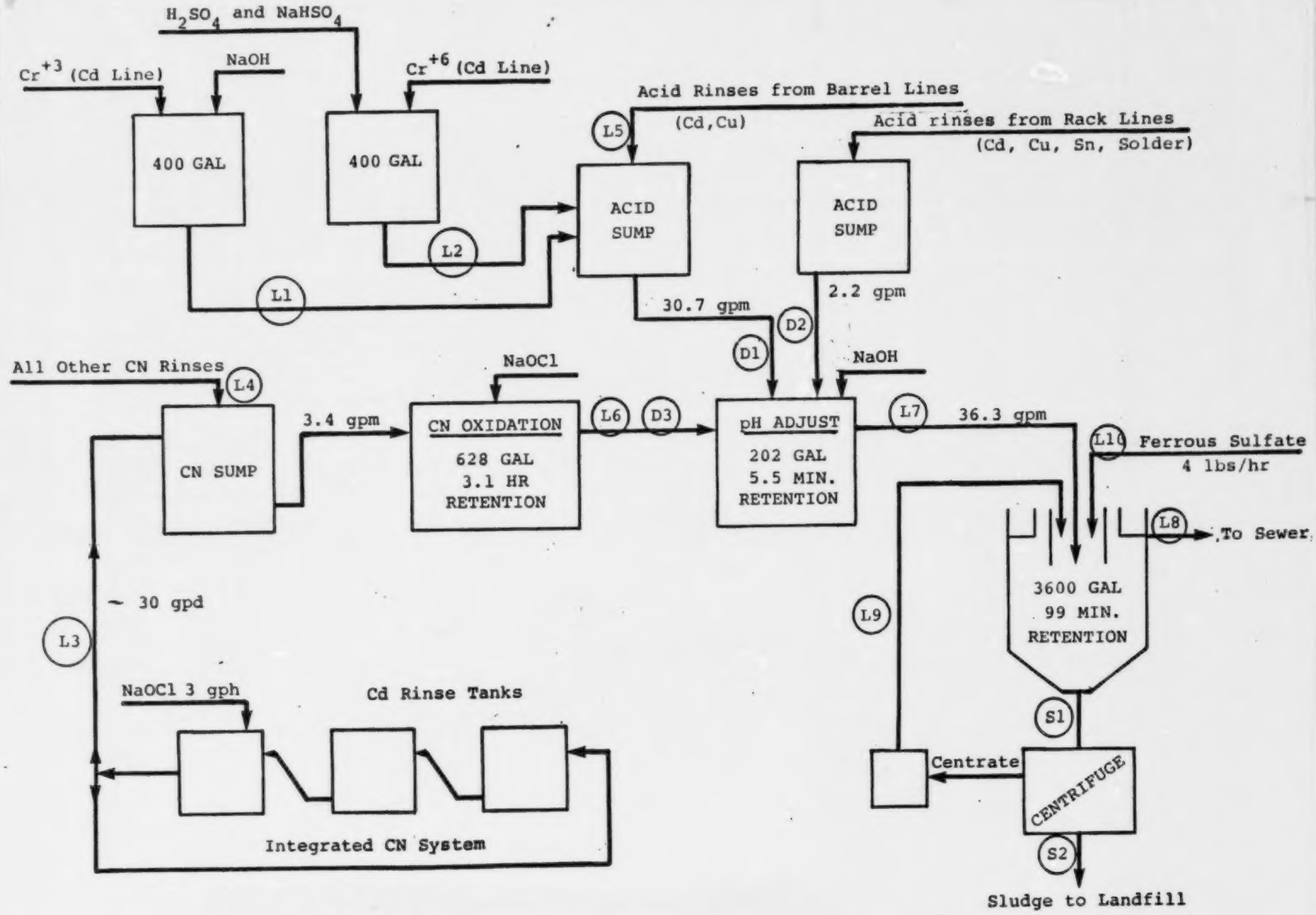
Plant 3B operates 13.5 hours per day, 5 days per week, with the majority of work performed during the first nine hours. The plant uses the same water saving techniques as plant 3A. The waste treatment facility operates 24 hours per day. Cadmium-cyanide wastewaters from barrel plating go through an integrated cyanide oxidation. Rinsewater containing sodium hypochlorite is constantly being bled off for further cyanide oxidation. Therefore, the rinsewater is also being replenished with fresh sodium hypochlorite at a rate of three gallons per hour. A cyanide collection sump receives these wastewaters along with cyanide rinsewater from all other plating. Cyanide oxidation for the combined cyanide streams is identical to plant 3A. Spent chromate solution is batch treated in an agitated tank with caustic for trivalent chromium, and sodium bisulfate and sulfuric acid for hexavalent chromium. After treatment, the solution is added to an acid sump and undergoes further treatment along with the acidic wastes as in plant 3A. pH adjusted wastewater overflows into a 3,500 gallon clarifier. Ferrous sulfate is added to the clarifier at the rate of 4 lbs per hour to complex any free cyanide. Clarifier overflow goes to the sewer while the sludge goes to a centrifuge for further dewatering. The centrifuge extract goes to a surge tank and is then recycled to the clarifier. Approximately 1,000 gallons per month of sludge are produced. Sludge is stored in drums until enough accumulates for hauling to a landfill. Iron sulfate for the clarifier is prepared by adding 50 lbs to 70 gallons of water.

Only plant 3B was sampled as this was the shop used in the original AES/EPA study. Sampling included: one 55-gallon drum of treated cyanide wastewater; 2 drums of acidic wastewater; one 2-1/2 gallon container of sludge before the centrifuge; two 2-1/2 gallon containers of sludge after the centrifuge; one liter samples of treated and untreated cyanide wastewaters, treated and untreated chromate, pH adjusted wastewater, and plant effluent.

PLANT #3

Discussion

Upon arrival of the sampling team, the plant had been operating at standard production rates for over 3 hours. The wastewater


H_2SO_4 and $NaHSO_4$
Cr^{+3} (Cd Line)
NaOH
Cr^{+6} (Cd Line)
400 GAL
400 GAL
L1
L2
L5
Acid Rinses from Barrel Lines
(Cd,Cu)
ACID SUMP
Acid rinses from Rack Lines
(Cd, Cu, Sn, Solder)
ACID SUMP
30.7 gpm
2.2 gpm
D1
D2
NaOH
All Other CN Rinses
L4
CN SUMP
3.4 gpm
NaOCl
CN OXIDATION
628 GAL
3.1 HR
RETENTION
L6
D3
pH ADJUST
202 GAL
5.5 MIN.
RETENTION
L7
36.3 gpm
L10
Ferrous Sulfate
4 lbs/hr
L8
To Sewer
3600 GAL
99 MIN.
RETENTION
L9
S1
Centrate
CENTRIFUGE
S2
Sludge to Landfill
~ 30 gpd
L3
NaOCl 3 gph
Cd Rinse Tanks
Integrated CN System

Plant #3 - Wastewater Treatment System for Copper and Cadmium Plating on Steel, Brass, and Copper

EPA Form 2350-4 (4-80)
(PREVIOUSLY C/N EPA FORM 287)
TYPING GUIDE SHEET

treatment system was, therefore, functioning under its normal operating conditions. All samples were grab samples. Liter samples were cooled and received by the laboratory the next day. Drum samples were not cooled and arrived seven days later. Flow rates were determined by measuring the dimensions of the sump tanks, shutting off the sump pumps, noting the rate at which the sump tanks filled and making the appropriate calculations. Retention times were determined by calculating the tank volume and dividing by the flow rate of wastewater. The locations of samples collected from the treatment system are shown on the attached diagram. Also shown are significant flow rates, tank volumes, and retention times.

Specific Notes

The chrome treatment is a batch system and only when treated (about once a week) are the tanks bled into the acid sump tank. This bleeding was taking place during the sampling.

The bleed from the integrated cyanide system runs to the CN sump in slugs of about 10 gallons. To the best of our knowledge this did not occur during the sampling period.

Total flow of wastewater amounted to 2,178 gph which corresponds well with plant estimates of 2,000 gph.

PLANT #4--FIRST VISIT

Plant #4 plates copper-nickel-chromium on zinc die-castings (primarily automotive trim). The plant, which currently employs about 110 people, includes one manual rack line The wastewater treatment system is composed of large batch treatment tanks which are manually controlled. No flows reach the treatment system over the weekend but cooling water does enter the pH-adjusted tank during the night. Cyanide is batch treated for about 2.5 to 3 hours; then a portion of the cyanide wastewaters are transferred to the pH adjustment tank. Nickel rinses and cleaner dumps are fed directly to the pH adjustment tank. The pH is adjusted to 10.4 and the waters are then pumped to the clarifier. Once a day the clarifier underflow is dropped to a holding tank. Approximately 10-12,000 gallons of sludge at about 3% solids are generated per month. Clarifier overflow is directed to percolating ponds on plant property.

The plant is currently having problems with nickel getting into the cyanide treatment system. To prevent this and also to protect the total system from dumps hitting it in slugs, the plant is installing some segregated sump tanks which will allow the operator to control the rates that different streams are treated.

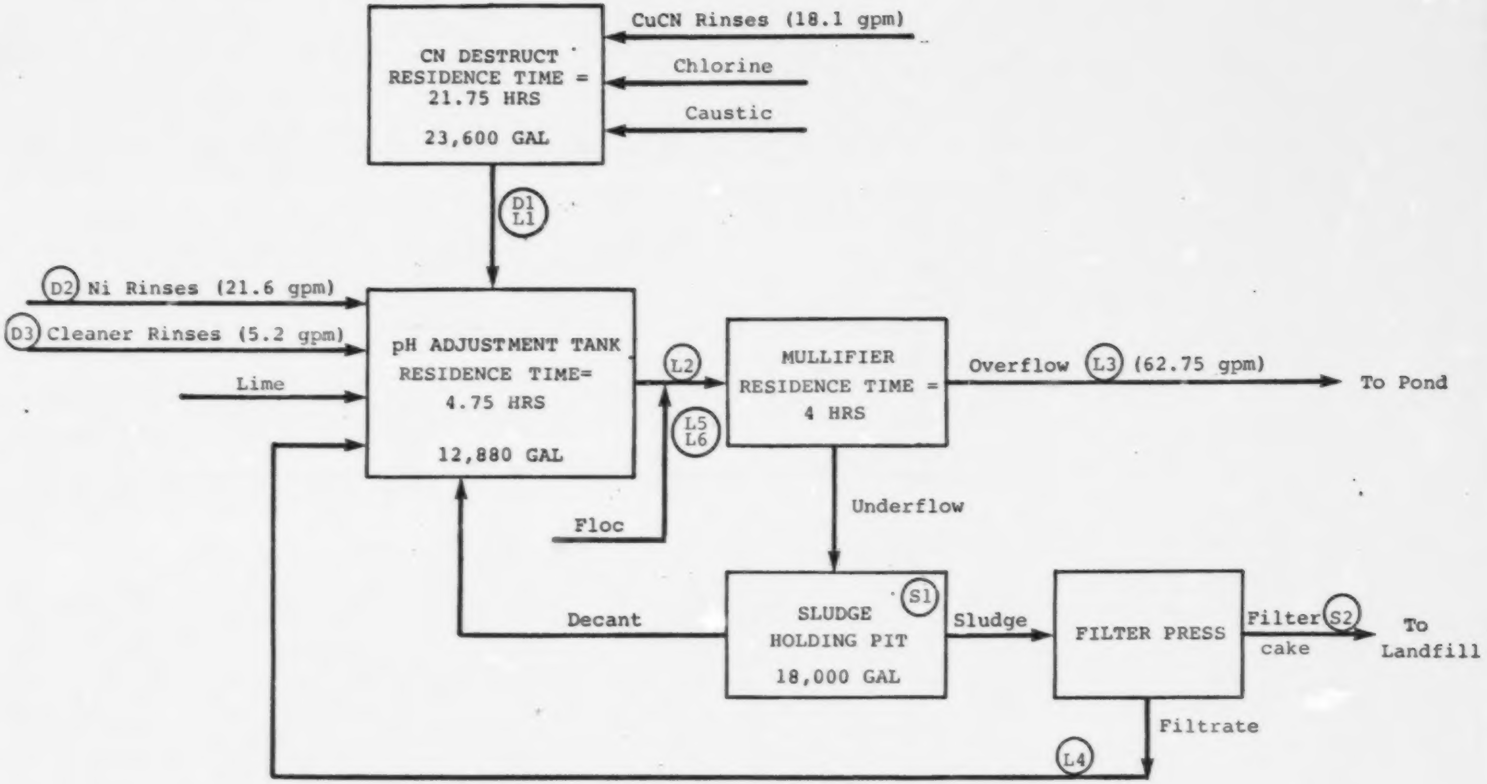
A plant-and-frame type filter is also being added after the clarifier to reduce sludge disposal costs. Sampling will take place after the system modifications have been made. Upon receipt of a diagram of the new system plus additional data from the plant, a detailed sampling plan will be prepared.

PLANT #4--SECOND VISIT

Upon arrival of the sampling team, the plant had been operating for three hours. The wastewater treatment system was therefore functioning under its normal operating conditions. There were no spills or dumps during the time we were sampling. All samples were grab samples. One-quart and half-gallon samples were air freighted and received at the laboratory on July 10. Drum samples were shipped by truck and received at the laboratory on July 16.

Rinse water flows that did not have flow limiting orifices were determined by displacement tests or by direct measurement into a bucket followed by the appropriate calculations. The attached diagram shows the wastewater flow rates, the tank volumes and retention times. It was not possible to allow for retention times when obtaining samples.

The plant uses 18 rinses that include still, overflow, closed-loop, and cascading rinse tanks. Flow restrictors were used on only three rinse tanks. The copper cyanide rinsewater flowrate was calculated to be 18.1 gpm. Cyanides are semi-continuously treated with liquid chlorine and 50% caustic in a continuously circulated tank. Caustic is added under pH control to maintain a minimum pH of 10. Chlorine flow is regulated by a chlorinator. However, the chlorinator is not calibrated so a flowrate could not be determined. An ORP meter is used to measure chlorine and has a set point of 600 mV. Cyanide oxidation is


CuCN Rinses (18.1 gpm)
Chlorine
Caustic
CN DESTRUCT
RESIDENCE TIME =
21.75 HRS
23,600 GAL
D1
L1
D2 Ni Rinses (21.6 gpm)
D3 Cleaner Rinses (5.2 gpm)
Lime
pH ADJUSTMENT TANK
RESIDENCE TIME=
4.75 HRS
12,880 GAL
L2
L5
L6
Floc
MULLIFIER
RESIDENCE TIME =
4 HRS
Overflow
L3
(62.75 gpm)
To Pond
Underflow
Decant
SLUDGE
HOLDING PIT
18,000 GAL
S1
Sludge
FILTER PRESS
Filter
cake
S2
To
Landfill
Filtrate
L4

Plant #4 - Wastewater Treatment System for Copper, Nickel and Chromium Plating onto Zinc Castings tested for completion with the use of potassium iodide starch indicator paper. When cyanide oxidation was complete, the pH meter showed a pH of 9.1 and the ORP meter read 680 mV. The treated cyanide tank was then transferred to the pH adjustment tank. The pH adjustment tank also receives rinse water from cleaners and nickel baths. Cleaner rinse water and nickel rinse water were calculated to be 5.2 gpm and 21.6 gpm, respectively. pH adjustment is performed in an agitated tank with the addition of lime to maintain a pH of 10.5. As the reaction with lime is slow, the downstream pH decreases by 0.4 pH units. During sampling, a pH of 10.8 was read on the plant pH meter for the pH adjusted waste stream. Metering pumps feed flocculant at an unknown flowrate into the pH adjusted waste stream before it enters the mullifier. The flocculant is prepared from 1-1/3 cups of Separade P-3 granular flocculant with approximately 57.6 gallons of water. The plant tries to maintain the pH of its effluent between 8 and 10.5. During sampling, the plant pH meter indicated a pH of 10 for the plant effluent stream.

The residence time in the cyanide destruct tank, neglecting solids buildup, is 21.75 hours, while residence time for the pH adjustment tank is 4.75 hours. Residence time for the mullifier averages 4 hours.

All dumps and spills go to the pH adjustment tank. Dumps are presently made in batches, but in the future will be bled into the waste treatment system as holdup sumps are put into use. The combined waste streams from our measurements total 45 gpm while the flow recorder on the plant effluent showed a 63 gpm average for the day we sampled. The batch transferring of treated cyanide rinsewater as well as lime, chlorine, and caustic flows may account for part of the discrepancy.

PLANT #6--FIRST VISIT

This shop performs decorative plating of nickel-chromium onto steel. One automatic rack line is used for plating, and one manual rack line is used for stripping. The shop uses water saving techniques such as counter flow rinsing, spray rinsing, dragout tanks, and water flow restrictors on all running rinse tanks. Shop operation averages 16 hours per day, 5-1/2 days per week.

The waste treatment system operates 17-21 hours per day and is typical of systems handling segregated wastes. Chromium bearing rinse water is collected in a sump from which it is pumped through a 2-stage chromium reducing reactor. In the reactor, 98 percent sulfuric acid converts scrap iron into ferrous ions. The ferrous ions then react with hexavalent chromium to produce trivalent chromium. The pH is kept at 2-4 to prevent the precipitaton of ferric and trivalent chromium ions. After chrome reduction, the treated wastewater overflows into the neutralization tank. Chrome and nickel plating solutions are replenished. Spent sulfuric acid (65 gallons) from the plating line is disposed of daily while other spent acids (130 gallons) and alkaline stripping solutions (195 gallons) are disposed of monthly. These spent solutions are either dumped or bled slowly into an agitated mixing tank along with burnishing water from spills, boiler blowdown, soak cleaner (65 gallons every 3 weeks), and electro-cleaner (300 gallons every 3 weeks). This tank is intended to smooth out variations of the wastewater to the next tank. From the mix tank wastewater is pumped to an agitated neutralization tank where it is combined with the acidic rinse water streams. Lime is added to this tank although not under pH control. This tank overflows to another agitated mixing tank where flocculant is added. Overflow from this tank enters a clarifier. The wastewater entering the clarifier contains roughly 15 percent (volume) suspended solids. Overflow from the clarifier is treated in another tank with sulfuric acid to maintain a pH of 7-10 and is finally discharged to the river. Another pH meter monitors the final effluent which varies between 28-32 gpm. The clarifier has a flat bottom and therefore contains a bottom trolley to rake sludge that is then transferred to a thickening tank. Sludge from this tank is pumped to a vacuum belt filter. The filter cake is hauled away in 300 gallon batches for disposal while the filtrate is recycled back to the first mixing tank.

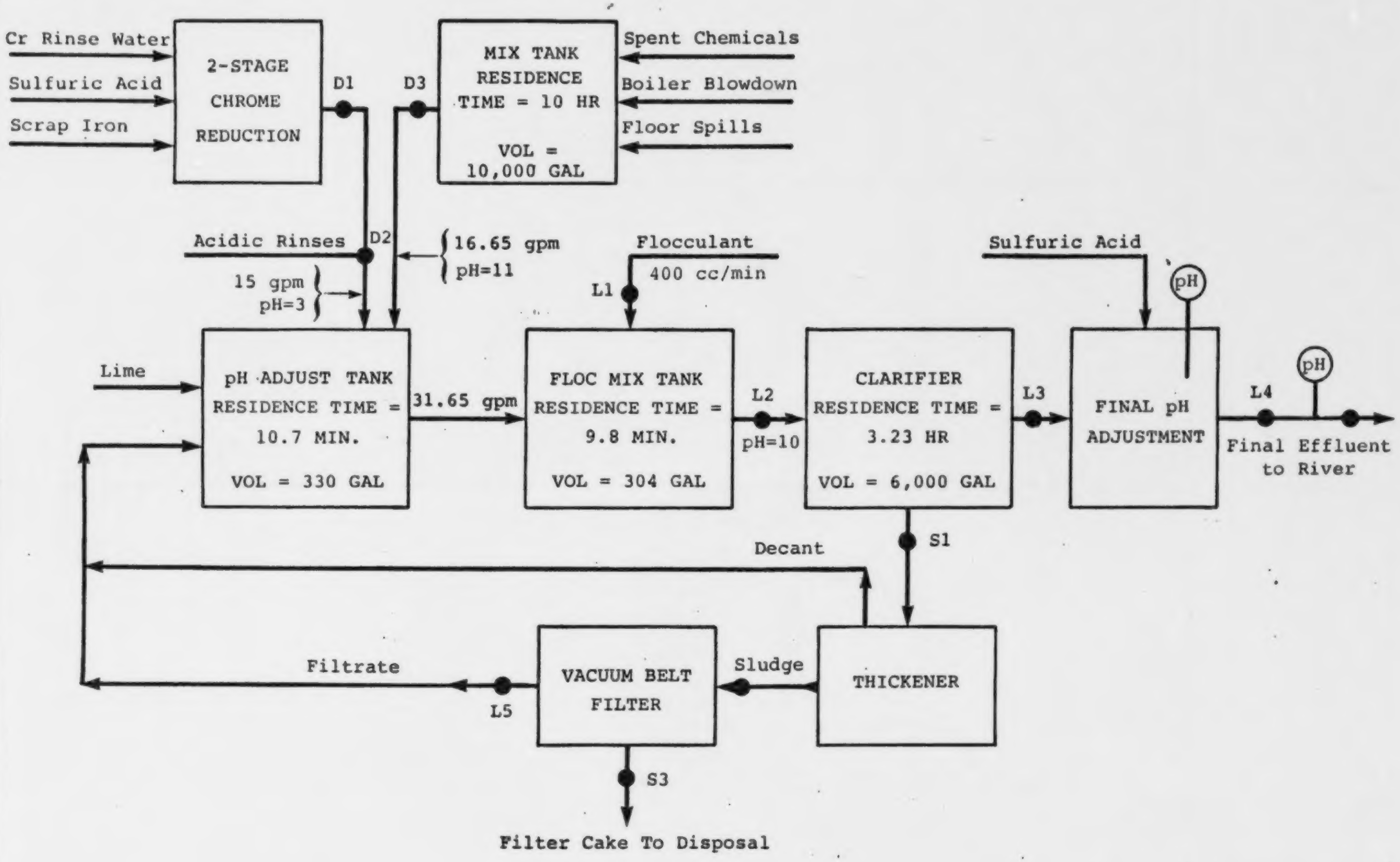
PLANT #6--SECOND VISIT

Discussion

Upon arrival of the sampling team, the plant had been operating for 4 hours. The wastewater treatment system was, therefore, functioning under its normal operating conditions. There were no spills or dumps during the time we were sampling. All samples were grab samples. One-quart and half-gallon samples were air shipped and received by the laboratory the next day. Drum samples were shipped by truck and should arrive at the laboratory by August 21.

Water flows that were not controlled by flow limiting orifices were determined by measuring the amount of time it took to fill a calibrated bucket. On the attached diagram are shown the wastewater flow rates, tank volumes and retention times. Samples were obtained, when possible, after allowing for the retention time in each tank.

The two acidic waste streams combine in the plant sewer and so separate samples could not be obtained. This fact corresponds to sample points D1 and D2 in the wastewater treatment diagram. Instead, a one-quart sample was obtained at D1 and a combined sample was used for D2. The flowrate of the combined acidic waste stream was 15 gpm as determined from flow restrictors. The flowrate of the alkaline waste stream was measured and found to be 16.7 gpm. The acidic and alkaline waste streams are both added to the pH adjustment tank. The residence time in this



Cr Rinse Water
Sulfuric Acid
Scrap Iron
2-STAGE CHROME REDUCTION
D1
D3
MIX TANK RESIDENCE TIME = 10 HR
VOL = 10,000 GAL
Spent Chemicals
Boiler Blowdown
Floor Spills
Acidic Rinses
D2
15 gpm
pH=3
16.65 gpm
pH=11
Lime
pH ADJUST TANK RESIDENCE TIME = 10.7 MIN.
VOL = 330 GAL
31.65 gpm
Flocculant
400 cc/min
L1
FLOC MIX TANK RESIDENCE TIME = 9.8 MIN.
VOL = 304 GAL
L2
pH=10
CLARIFIER RESIDENCE TIME = 3.23 HR
VOL = 6,000 GAL
L3
Sulfuric Acid
pH
FINAL pH ADJUSTMENT
L4
pH
Final Effluent to River
S1
Decant
THICKENER
Sludge
VACUUM BELT FILTER
Filtrate
L5
S3
Filter Cake To Disposal

Plant #6 - Wastewater Treatment System for Nickel and Chrome Plating onto Steel tank is 10.7 minutes. As the variability of the waste stream flowrates is very small, the lime addition rate is manually adjusted when necessary. The overflow from the pH adjust tank goes into the floc mixing tank. The residence time in this tank is 9.8 minutes. Flocculant is purchased in granular form and mixed at the rate of 12 oz. powder to 50 gallons of total solution. The flocculant brand name is Percol. The flocculant solution is added at the rate of 400 cc/min. Overflow from the floc mixing tank enters the clarifier. Residence time in the clarifier is 3.23 hours. The vacuum belt filter was shut down around 11:45 due to mechanical problems. Therefore, samples of the sludge from the thickener and filtrate from the filter could not be obtained.

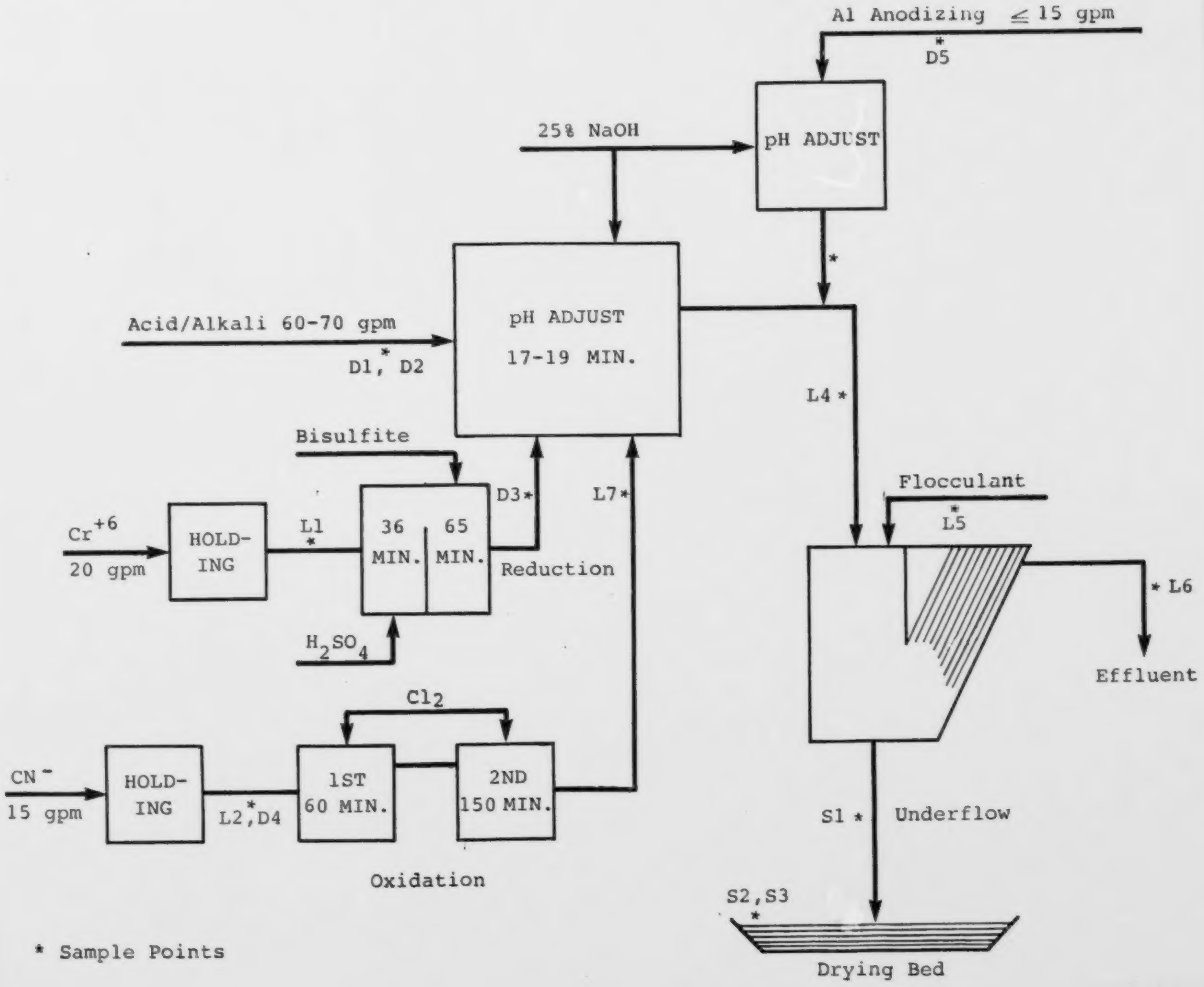
PLANT #7

Plant Operation

For this trip, sampling started at 2:40 p.m. and finished at 5:30 p.m. Production rate was at 100 percent (no details given) and the following plating lines were in operation:

Nickel	2-Barrel	
Zinc	2-Barrel	2-Rack
Copper	1-Barrel	
Brass	1-Line	
Anodizing	3-Lines	
Bright Dip	2-Lines	
Chrome	1-Line	

Bronze, cadmium and black chrome product lines were not in operation.


Al Anodizing ≤ 15 gpm
D5*
25% NaOH
pH ADJUST
*
Acid/Alkali 60-70 gpm
D1*, D2
pH ADJUST
17-19 MIN.
L4 *
Bisulfite
Cr+6
20 gpm
HOLD-ING
L1*
36 MIN.
65 MIN.
D3*
L7*
Reduction
H2SO4
Flocculant
L5*
* L6
Effluent
Cl2
CN-
15 gpm
HOLD-ING
L2*, D4
1ST 60 MIN.
2ND 150 MIN.
Oxidation
S1 *
Underflow
S2, S3*
Drying Bed
* Sample Points

Plant #7 - Wastewater Treatment System

All accidental and normal dumps and spills go to the acid/alkali sewer. Chrome and cyanide spills, therefore, do not undergo their separate treatments. There were no abnormal spills during the sample period, but there was a routine dump of chromic acid and sodium bichromate. Chromate dumping routinely takes place four times a day.

To the best of his knowledge, the plant manager thinks that 10 gallons of water are added to one gram of flocculant. The plant uses Hercofloc™, manufactured by Hercules. Approximately 400 gallons of flocculant solution is fed in a 24-hour period. The feedrate was determined at one time to match the plant's requirements and has not been changed since. Flocculant is fed continuously to the clarifier.

Retention times and flowrates for each treatment step is shown on the accompanying effluent flow diagram. The feedrate of separate effluent streams to treatment is fairly independent of production rate, as we noticed rinsewater running on lines that were not operating. Fifty-nine rinse tanks were counted for the plating and anodizing lines that were operating. As all of these are supposed to have flow restrictors, we assumed an additional 0.5 gpm above the 1.0 gpm per rinse to account for wear and poor operation for a 90 gpm total. Then adding 30 gpm for cooling water, condensate and miscellaneous, total flow comes to 120 gpm. This agrees well with the 117.6 gpm from flow meter data on the September 23 trip. By measurement, the cyanide sump pump delivered 24.6 gpm and was actually running 42.3 percent of the time. This averaged out to be 10.3 gpm. The chromium sump pump delivered 54.6 gpm and was actually running 21.3 percent of the time. This averaged out to 11.6 gpm. Both pumps were activated by floats in the sump. By all the above methods, wastewater flow is somewhere between 100 and 120 gpm.

SAMPLING PROCEDURE

The table below outlines the sampling sequence and data collected during the plant visit.

Time	Work Performed	Data
2:40-2:46	Collected two drums of acid/alkali waste prior to pH adjustment at D-1 and D-2. pH was determined by pH paper.	pH = 6.5
2:58-3:00	Collected one drum of chromium waste at outlet of 2nd stage treatment at D-3. pH + ORP reading from plant instruments was located at inlet to 2nd stage. pH of drum sample made by pH paper.	pH of drum sample = 1.0 pH recorder = 2-3.4 pH set point = 3.0 pH indicator = 3.0 ORP recorder = 2-2.4mv ORP set pt. = 3.0 mv ORP indicator = 3.2 mv
3:40-3:45	Collected one drum of Aluminum anodizing waste at D-5. Checked pH of drum sample with pH paper.	pH = 3.0
3:55	Collected one qt sample of clarifier overflow at L-6.	pH = 9.0
4:05	Collected one qt sample of flocculant solution fed to clarifier at L-5.	pH = 5.5
4:06	Collected one qt sample of combined plant effluent fed to clarifier at L-4.	pH = 7.0

One explanation as to clarifier overflow being slightly alkaline while feed and flow are neutral and slightly acid is that sometime before we sampled, the feed must have been highly alkaline and much of it was still in the clarifier. The pH of clarifier underflow was not checked.

Time	Work Performed	Data
4:15-4:25	Collected two 2-1/2 gal. jugs of moist sludge (S-2, S-8)	
4:17	Collected one 2-1/2 gal. jug of clarifier underflow at S-1.	
4:27	Collected one qt sample of cyanide waste at influent to first stage oxidation at L-2.	pH = 8.5
	Collected one qt sample of caustic solution used in plant at L-3.	
4:30	Collected one qt sample of chromium waste prior to reduction at L-1.	pH = 2.0
4:32	Collected three one qt samples of treated cyanide wste at L-7.	pH = 6.5
4:40-4:45	Collected one drum of untreated cyanide at D-4. This sample is the same as L-2.	pH = 6.5

Due to the retention times in the various cyanide waste holdup and treatment tanks, a drum sample of untreated cyanide instead of treated cyanide was collected. The reason for this is that earlier in the day a bucket of cadmium cyanide was purposely dumped into the cyanide sewer so there would be some cadmium in the waste we sampled. As mentioned earlier, due to retention times, the cadmium takes quite a while to go through the system and we could wait no longer. It was assumed that the lab could chlorinate the drum sample so that it would resemble treated cyanide waste at L-7.

5:15-5:30	Took reading of effluent pH which leaves the plant. Took readings of neutralizer pH of waste from plating shop.	pH = 7.8 pH set point = 9 pH indicator not working pH recorder not working

Cyanide Sump = 51 gallons/inch
when pump is off, fill rate = 5.25" in 15 minutes
when pump is on, emptying rate = 5.25" in 11 minutes

Chromium Sump = 39 gallons/inch
when pump is off, fill rate = 9" in 18.5 minutes
when pump is on, emptying rate = 7" in 5 minutes

Cyanide Tank:

1st stage	4' x 5' x 6'	= 900 gallons
2nd stage	10' x 5.5' x 5.5'	= 2260 gallons

Chromium Tank:

1st stage	4' x 4' x 6'	= 720 gallons
2nd stage	4' x 8' x 5.5'	= 1315 gallons

Neutralization Tank 6' x 10' x 4' = 1800 gallons

PLANT #8--FIRST VISIT

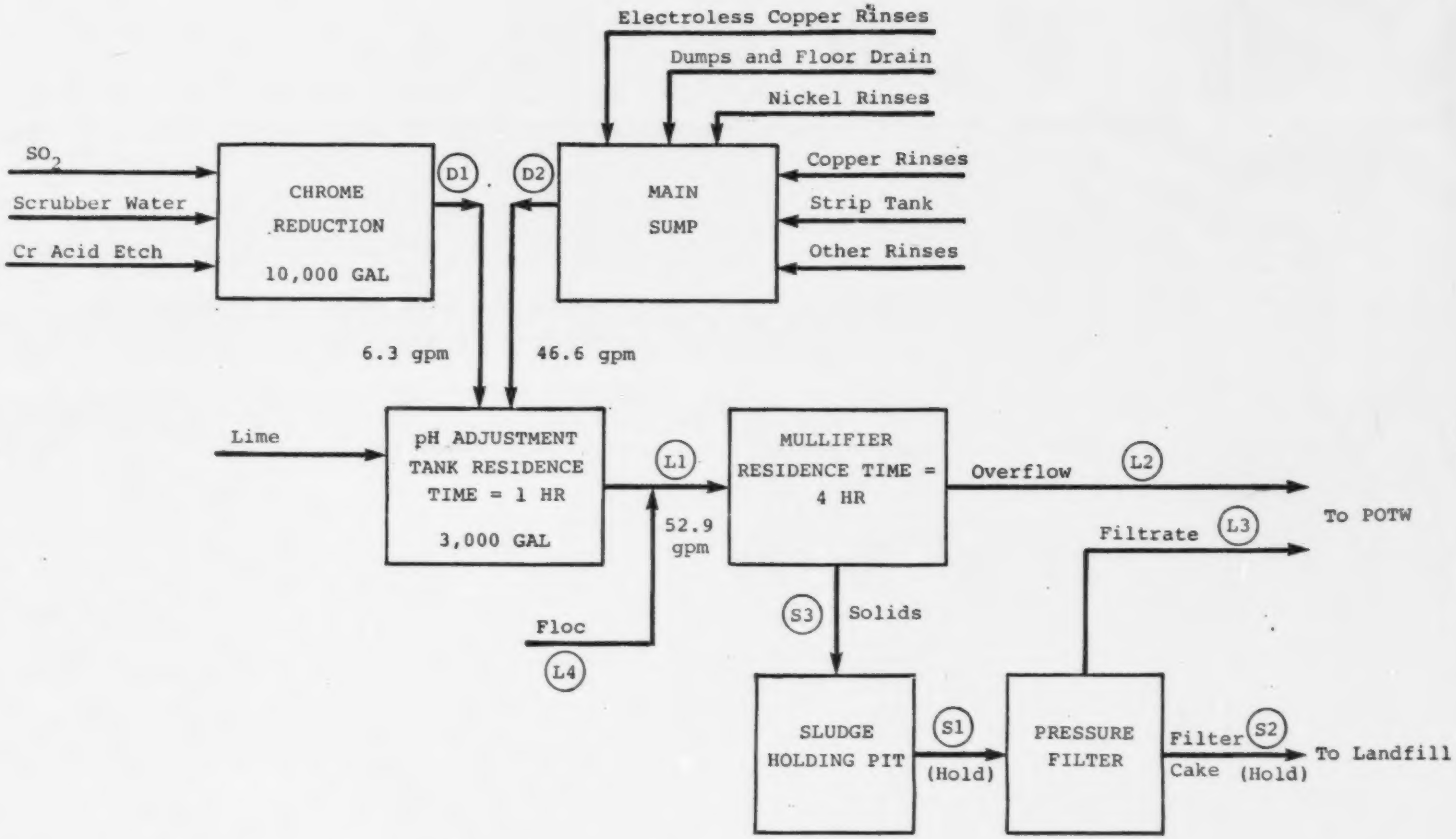
Plant #8 plates copper-nickel-chromium on ABS plastic. The system is composed of one manual rack plating line. The parts to be plated (primarily automotive trim) go through the following operations (plus appropriate rinses): chromic acid etch; catalyst dip (palladium); accelarator dip; electroless copper; copper strike; acid copper; dull nickel; bright nickel; chromium. Waste rinse waters are routed to sumps which are eventually pumped to the wastewater treatment system. The diagram illustrates the system of wastewater sumps and treatment. When dumps occur, they go first to the strip sump and are then pumped to the nickel sump and from there to the main sump. Most chromium rinses go to evaporative recovery and the concentrate is used in the chromic acid etch tanks. Some chromium does, however, go directly to the chromium reduction system.

The treatment system operates 24 hours a day. Plating operations start at 5:30 a.m. and continue for 16 to 20 hours, 4 days a week. Based on a 20-hour day, wastewaters flows average 72,900 gallons, with a maximum of 98,820 and a minimum of 72,900. The plant has flow restrictors on all flowing rinse tanks. There are no countercurrent rinses on this line. Effluent goes directly to the POTW which is located near to the plant. A recent effluent analysis showed the following: $Cr^T = 1.0$ ppm; Cu = 1.6 ppm; Ni = 1.0 ppm. No cyanide is used at this plant.

PLANT #8--SECOND VISIT

Discussion

Upon arrival of the sampling team, the plant had been operating for 4 hours. The wastewater treatment system was therefore functioning under its normal operating conditions. There were no spills or dumps during the time we were sampling. All samples were grab samples. One-quart and half-gallon samples were air freighted and received by the laboratory the next day. Drum samples were shipped by truck and should arrive at the laboratory by July 24.


SO$_2$
Scrubber Water
Cr Acid Etch
CHROME REDUCTION 10,000 GAL
D1
D2
Electroless Copper Rinses
Dumps and Floor Drain
Nickel Rinses
Copper Rinses
Strip Tank
Other Rinses
MAIN SUMP
6.3 gpm
46.6 gpm
Lime
pH ADJUSTMENT TANK RESIDENCE TIME = 1 HR 3,000 GAL
L1
52.9 gpm
Floc
L4
MULLIFIER RESIDENCE TIME = 4 HR
Overflow
L2
To POTW
Filtrate
L3
S3
Solids
SLUDGE HOLDING PIT
S1
(Hold)
PRESSURE FILTER
Filter Cake
S2
(Hold)
To Landfill

Plant #8 - Wastewater Treatment System for Plating Copper, Nickel onto Plastic

Water flows, to rinses not controlled by flow limiting orifices, were determined by measuring rinse tank overflows and spray nozzles directly into a calibrated vessel, and making the appropriate calculations. The attached diagram shows the wastewater flow rates, tank volumes and retention times. Samples were obtained when possible, after allowing for the retention time in each tank.

Plant personnel were cooperative and provided substantial assistance during the collection of samples. Copies of the analytical results generated by this study were promised to plant personnel when they are available.

The plant uses 23 rinses that include still, overflow, closed-loop, and cascading rinse tanks. Flow restrictors were used on all but three rinse tanks. The total reduced chromium waste stream was calculated to be 6.3 gpm. This includes 2.7 gpm of scrubber water added to the chromium sump. Chromium is treated with gaseous sulfur dioxide in a continuously circulated pit. The treated chromium is transferred to the pH adjustment tank when the ORP meter reads 280 mV, and stops when the reading reaches 320 mV. The flowrate of cleaners and acidic rinses totals 46.63 gpm. This stream is transferred to the pH adjustment tank from the main sump. Lime slurry is added to the pH adjustment tank to maintain a pH of 8.8 to 9.2. The pH-adjusted waste stream is pumped to the mullifier when the level in the pH tank reaches its set point. Metering pumps feed diluted flocculant at a rate of 225 ml/min into the waste stream before it enters the mullifier. The plant maintains the pH of its effluent between 7 and 10. The residence time in the pH adjustment tank is approximately 1 hour, while residence time in the mullifier averages 4 hours.

All dumps and spills are routed to the main sump. Dumps are made in batches as surge tanks are not available. The combined waste streams totaled 52.93 gpm during our sampling; the treatment system is designed to handle 150 gpm. The treatment system operates 24 hours/day, 4 days/week, and 8 hours on the 5th day. The plating facility operates two 10-hour shifts, 4 days per week.

SECTION 8

DETAILED RESULTS OF THE STATISTICAL ANALYSIS OF THE SCREENING EXPERIMENTS

Two-way analysis of variance computations for each plant investigated are presented. In the case of Plant 7, where an experimental design involving partial replication was used, main effect and interaction sum of squares were obtained utilizing the mean of the replicated values presented in Tables 5-6 and 5-9. The error sum of squares was computed using the replicated data only. For all other plants, full replication was used and analysis of variance proceeded by standard methods.

In the tables which follow, DF = degrees of freedom, SS = sum of squares, MS = mean square, and F is the value of the F-statistic. The effects are designated by A = pH, B = chemical, AxB = interaction, E = error, and T = total. The AB effect is termed the treatment effect by analogy with one-way ANOVA. The treatment sum of squares is subdivided into its components, the main effect and the interaction sum of squares. While the treatment effect is not usually presented separately in ANOVA tables as is done here, some standard works do present it in this manner (e.g., Miller, I. and J. E. Freund, Probability and Statistics for Engineers, Prentice-Hall, Inc., NJ, 1977).

PLANT #2

FILTRATE

CHROMIUM - TOTAL

DF		SS	MS	F
11.	T	0.0		
5.	AB	0.0	0.0	1.0
1.	A	0.0	0.0	1.0
2.	B	0.0	0.0	1.0
2.	A×B	0.0	0.0	1.0
6.	E	0.0	0.0	

ZINC

DF		SS	MS	F
11.	T	9.1		
5.	AB	5.6	1.1	1.9
1.	A	2.2	2.2	3.8
2.	B	1.5	0.7	1.2
2.	A×B	1.9	1.0	1.7
6.	E	3.5	0.6	

CADMIUM

DF		SS	MS	F
11.	T	460.0		
5.	AB	443.1	88.6	31.4
1.	A	200.6	200.6	71.1
2.	B	119.3	59.7	21.1
2.	A×B	123.2	61.6	21.8
6.	E	16.9	2.8	

PLANT #2

EFFLUENT

CHROMIUM - TOTAL

DF		SS	MS	F
11.	T	0.6		
5.	AB	0.5	0.1	5.4
1.	A	0.1	0.1	5.5
2.	B	0.2	0.1	5.4
2.	A×B	0.2	0.1	5.4
6.	E	0.1	0.0	

ZINC

DF		SS	MS	F
11.	T	7.4		
5.	AB	5.2	1.0	2.8
1.	A	0.2	0.2	0.6
2.	B	1.6	0.8	2.2
2.	A×B	3.3	1.7	4.5
6.	E	2.2	0.4	

CADMIUM

DF		SS	MS	F
11.	T	152.0		
5.	AB	123.8	24.8	5.3
1.	A	64.7	64.7	13.8
2.	B	17.8	8.9	1.9
2.	A×B	41.3	20.6	4.4
6.	E	28.2	4.7	

PLANT #2

SLUDGE - EP

CHROMIUM - TOTAL

DF		SS	MS	F
11.	T	95636.5		
5.	AB	31892.1	6378.4	0.6
1.	A	2253.7	2253.7	0.2
2.	B	28817.3	14408.6	1.4
2.	A×B	821.2	410.6	0.0
6.	E	63744.4	10624.1	

ZINC

DF		SS	MS	F
11.	T	85179.7		
5.	AB	44407.7	8881.5	1.3
1.	A	1323.0	1323.0	0.2
2.	B	24760.2	12380.1	1.8
2.	A×B	18324.5	9162.3	1.3
6.	E	40772.0	6795.3	

CADMIUM

DF		SS	MS	F
11.	T	89846.3		
5.	AB	30516.8	6103.4	0.6
1.	A	8694.1	8694.1	0.9
2.	B	18531.5	9265.8	0.9
2.	A×B	3291.2	1645.6	0.2
6.	E	59329.5	9888.3	

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PLANT #3

FILTRATE

CHROMIUM - TOTAL

DF		SS	MS	F
11.	T	57.1		
5.	AB	32.9	6.6	1.6
1.	A	28.0	28.0	6.9
2.	B	4.1	2.0	0.5
2.	A×B	0.8	0.4	0.1
6.	E	24.2	4.0	

CHROMIUM - HEXAVALENT

DF		SS	MS	F
11.	T	184.8		
5.	AB	72.1	14.4	0.8
1.	A	10.6	10.6	0.6
2.	B	50.3	25.2	1.3
2.	A×B	11.3	5.6	0.3
6.	E	112.7	18.8	

CADMIUM

DF		SS	MS	F
11.	T	0.3		
5.	AB	0.2	0.0	3.3
1.	A	0.2	0.2	13.7
2.	B	0.0	0.0	0.8
2.	A×B	0.0	0.0	0.7
6.	E	0.1	0.0	

PLANT #3

EFFLUENT

CHROMIUM - TOTAL

DF		SS	MS	F
11.	T	45.4		
5.	AB	14.2	2.8	0.5
1.	A	12.0	12.0	2.3
2.	B	1.3	0.6	0.1
2.	A×B	0.9	0.4	0.1
6.	E	31.2	5.2	

CHROMIUM - HEXAVALENT

DF		SS	MS	F
11.	T	89.5		
5.	AB	27.5	5.5	0.5
1.	A	18.8	18.8	1.8
2.	B	2.7	1.4	0.1
2.	A×B	5.9	3.0	0.3
6.	E	62.0	10.3	

CADMIUM

DF		SS	MS	F
11.	T	11.6		
5.	AB	5.4	1.1	1.0
1.	A	0.1	0.1	0.1
2.	B	3.5	1.7	1.7
2.	A×B	1.9	0.9	0.9
6.	E	6.2	1.0	

PLANT #3

SLUDGE - EP

CHROMIUM - TOTAL

DF		SS	MS	F
11.	T	3.0		
5.	AB	1.4	0.3	1.1
1.	A	0.9	0.9	3.6
2.	B	0.5	0.2	0.9
2.	A×B	0.0	0.0	0.0
6.	E	1.6	0.3	

CHROMIUM - HEXAVALENT

DF		SS	MS	F
11.	T	5.0		
5.	AB	3.6	0.7	3.0
1.	A	0.9	0.9	3.7
2.	B	2.1	1.1	4.6
2.	A×B	0.6	0.3	1.2
6.	E	1.4	0.2	

CADMIUM

DF		SS	MS	F
11.	T	36113.0		
5.	AB	28363.0	5672.6	4.4
1.	A	3201.3	3201.3	2.5
2.	B	14773.5	7386.8	5.7
2.	A×B	10388.2	5194.1	4.0
6.	E	7750.0	1291.7	

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PLANT #4

FILTRATE

CHROMIUM - TOTAL

DF		SS	MS	F
11.	T	560.6		
5.	AB	253.8	50.8	1.0
1.	A	50.8	50.8	1.0
2.	B	98.8	49.4	1.0
2.	A×B	104.2	52.1	1.0
6.	E	306.8	51.1	

COPPER

DF		SS	MS	F
11.	T	117.8		
5.	AB	99.6	19.9	6.5
1.	A	11.3	11.3	3.7
2.	B	51.9	26.0	8.5
2.	A×B	36.3	18.2	6.0
6.	E	18.3	3.0	

NICKEL

DF		SS	MS	F
11.	T	1729.3		
5.	AB	1209.2	241.8	2.8
1.	A	694.6	694.6	8.0
2.	B	151.3	75.6	0.9
2.	A×B	363.3	181.6	2.1
6.	E	520.2	86.7	

PLANT #4

EFFLUENT

CHROMIUM - TOTAL

DF		SS	MS	F
11.	T	0.1		
5.	AB	0.1	0.0	1.6
1.	A	0.0	0.0	0.0
2.	B	0.1	0.0	3.3
2.	A×B	0.0	0.0	0.6
6.	E	0.1	0.0	

COPPER

DF		SS	MS	F
11.	T	93.1		
5.	AB	71.9	14.4	4.1
1.	A	9.2	9.2	2.6
2.	B	48.8	24.4	6.9
2.	A×B	14.0	7.0	2.0
6.	E	21.1	3.5	

NICKEL

DF		SS	MS	F
11.	T	1816.5		
5.	AB	1770.7	354.1	46.4
1.	A	1566.8	1566.8	205.2
2.	B	108.8	54.4	7.1
2.	A×B	95.0	47.5	6.2
6.	E	45.8	7.6	

PLANT #4

SLUDGE - EP

CHROMIUM - TOTAL

DF		SS	MS	F
11.	T	5.4		
5.	AB	2.9	0.6	1.4
1.	A	1.0	1.0	2.4
2.	B	1.2	0.6	1.5
2.	A×B	0.7	0.3	0.8
6.	E	2.5	0.4	

COPPER

DF		SS	MS	F
11.	T	1216385.4		
5.	AB	1053520.7	210704.1	7.8
1.	A	760536.8	760536.8	28.0
2.	B	69050.3	34525.1	1.3
2.	A×B	223933.6	111966.8	4.1
6.	E	162864.8	27144.1	

NICKEL

DF		SS	MS	F
11.	T	1360380.3		
5.	AB	1197053.8	239410.8	8.8
1.	A	111168.8	111168.8	4.1
2.	B	495550.5	247775.3	9.1
2.	A×B	590334.5	295167.3	10.8
6.	E	163326.5	27221.1	

PLANT #6

FILTRATE

CHROMIUM - TOTAL

DF		SS	MS	F
11.	T	0.0		
5.	AB	0.0	0.0	0.8
1.	A	0.0	0.0	0.6
2.	B	0.0	0.0	0.4
2.	A×B	0.0	0.0	1.2
6.	E	0.0	0.0	

NICKEL

DF		SS	MS	F
11.	T	0.0		
5.	AB	0.0	0.0	1.0
1.	A	0.0	0.0	0.9
2.	B	0.0	0.0	0.9
2.	A×B	0.0	0.0	1.1
6.	E	0.0	0.0	

PLANT #6

EFFLUENT

CHROMIUM - TOTAL

DF		SS	MS	F
11.	T	23.6		
5.	AB	15.3	3.1	2.2
1.	A	2.9	2.9	2.1
2.	B	6.7	3.3	2.4
2.	A×B	5.7	2.9	2.1
6.	E	8.3	1.4	

NICKEL

DF		SS	MS	F
11.	T	0.7		
5.	AB	0.4	0.1	2.2
1.	A	0.0	0.0	0.1
2.	B	0.3	0.1	3.2
2.	A×B	0.2	0.1	2.3
6.	E	0.2	0.0	

PLANT #6

SLUDGE - EP

CHROMIUM - TOTAL

DF		SS	MS	F
11.	T	50.2		
5.	AB	47.1	9.4	17.9
1.	A	29.0	29.0	55.2
2.	B	10.2	5.1	9.7
2.	A×B	7.8	3.9	7.5
6.	E	3.2	0.5	

NICKEL

DF		SS	MS	F
11.	T	1949.9		
5.	AB	1396.2	279.2	3.0
1.	A	646.8	646.8	7.0
2.	B	55.5	27.8	0.3
2.	A×B	693.9	347.0	3.8
6.	E	553.6	92.3	

PLANT #7

EFFLUENT

	SS	DF	MS	F
Cadmium				
Chemical	.000439	2	.0002195	1.316
pH	.01417	2	.007086	42.516
Interaction	.00069	4	.000173	1.042
Error	.000498	3	.000166	
Chromium				
Chemical	.014317	2	.00716	3.767
pH	.044517	2	.02226	11.72
Interaction	.025916	4	.006479	3.41
Error	.0057	3	.0019	
Copper				
Chemical	.000072	2	.000036	1.08
pH	.001172	2	.000586	17.58
Interaction	.000461	4	.00011525	3.459
Error	.0001	3	.0000333	
Nickel				
Chemical	.20829	2	.10445	.245
pH	84.59936	2	42.29968	99.38
Interaction	.49689	4	.12422	.292
Error	1.27695	3	.42565	
Zinc				
Chemical	.27782	2	.13891	1.054
pH	3.8743	2	1.93715	14.703
Interaction	1.64379	4	.41095	3.119
Error	.39525	3	.13175	

PLANT #7

SLUDGE - ASTM

	SS	DF	MS	F
		Cadmium		
Chemical	.0016889	2	.0008445	.259
pH	.0021555	2	.0010778	.330
Interaction	.001376	4	.000344	.106
Error	.0098	3	.0032667	
		Chrome		
Chemical	.01477	2	.00739	.813
pH	.07157	2	.03579	3.939
Interaction	.083313	4	.02083	2.293
Error	.02725	3	.00908	
		Copper		
Chemical	.64229	2	.32114	2.180
pH	.97176	2	.48588	3.300
Interaction	1.50486	4	.37622	2.555
Error	.44175	3	.14725	
		Nickel		
Chemical	44.1187	2	22.0594	2.109
pH	114.0898	2	57.0449	5.46
Interaction	86.3916	4	21.5979	2.064
Error	31.38125	3	10.4604	
		Zinc		
Chemical	7.15917	2	3.57959	.254
pH	23.5395	2	11.76975	.833
Interaction	15.6077	4	3.90193	.276
Error	42.38885	3	14.12962	

PLANT #8

FILTRATE

CHROMIUM - TOTAL

DF		SS	MS	F
11.	T	109.6		
5.	AB	108.1	21.6	85.4
1.	A	21.6	21.6	85.3
2.	B	47.5	23.7	93.8
2.	A×B	39.0	19.5	77.1
6.	E	1.5	0.3	

COPPER

DF		SS	MS	F
11.	T	1.5		
5.	AB	1.3	0.3	9.8
1.	A	0.0	0.0	0.1
2.	B	0.9	0.5	17.5
2.	A×B	0.4	0.2	6.9
6.	E	0.2	0.0	

NICKEL

DF		SS	MS	F
11.	T	0.1		
5.	AB	0.1	0.0	4.0
1.	A	0.1	0.1	11.1
2.	B	0.0	0.0	2.6
2.	A×B	0.0	0.0	1.9
6.	E	0.0	0.0	

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PLANT #8

EFFLUENT

CHROMIUM - TOTAL

DF		SS	MS	F
11.	T	126507.1		
5.	AB	111363.8	22272.8	8.8
1.	A	17879.5	17879.5	7.1
2.	B	56218.0	28109.0	11.1
2.	A×B	37266.4	18633.2	7.4
6.	E	15143.3	2523.9	

COPPER

DF		SS	MS	F
11.	T	3119.4		
5.	AB	3107.6	621.5	316.1
1.	A	603.9	603.9	307.1
2.	B	1303.0	651.5	331.3
2.	A×B	1200.7	600.3	305.3
6.	E	11.8	2.0	

NICKEL

DF		SS	MS	F
11.	T	2898.1		
5.	AB	2820.0	564.0	43.3
1.	A	496.0	496.0	38.1
2.	B	1324.5	662.3	50.8
2.	A×B	999.4	499.7	38.4
6.	E	78.2	13.0	

PLANT #8

SLUDGE - EP

CHROMIUM - TOTAL

DF		SS	MS	F
11.	T	605920.7		
5.	AB	379275.4	75855.1	2.0
1.	A	5055.3	5055.3	0.1
2.	B	369074.7	184537.3	4.9
2.	A×B	5145.4	2572.7	0.1
6.	E	226645.3	37774.2	

COPPER

DF		SS	MS	F
11.	T	1319.9		
5.	AB	1082.3	216.5	5.5
1.	A	356.6	356.6	9.0
2.	B	395.3	197.6	5.0
2.	A×B	330.4	165.2	4.2
6.	E	237.5	39.6	

NICKEL

DF		SS	MS	F
11.	T	45271.5		
5.	AB	39292.1	7858.4	7.9
1.	A	262.3	262.3	0.3
2.	B	34536.8	17268.4	17.3
2.	A×B	4493.0	2246.5	2.3
6.	E	5979.4	996.6	

SECTION 9

GRAPHS OF METAL CONTENT IN CLARIFIER OVERFLOWS AND SLUDGE FILTRATE FROM SCREENING TESTS

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

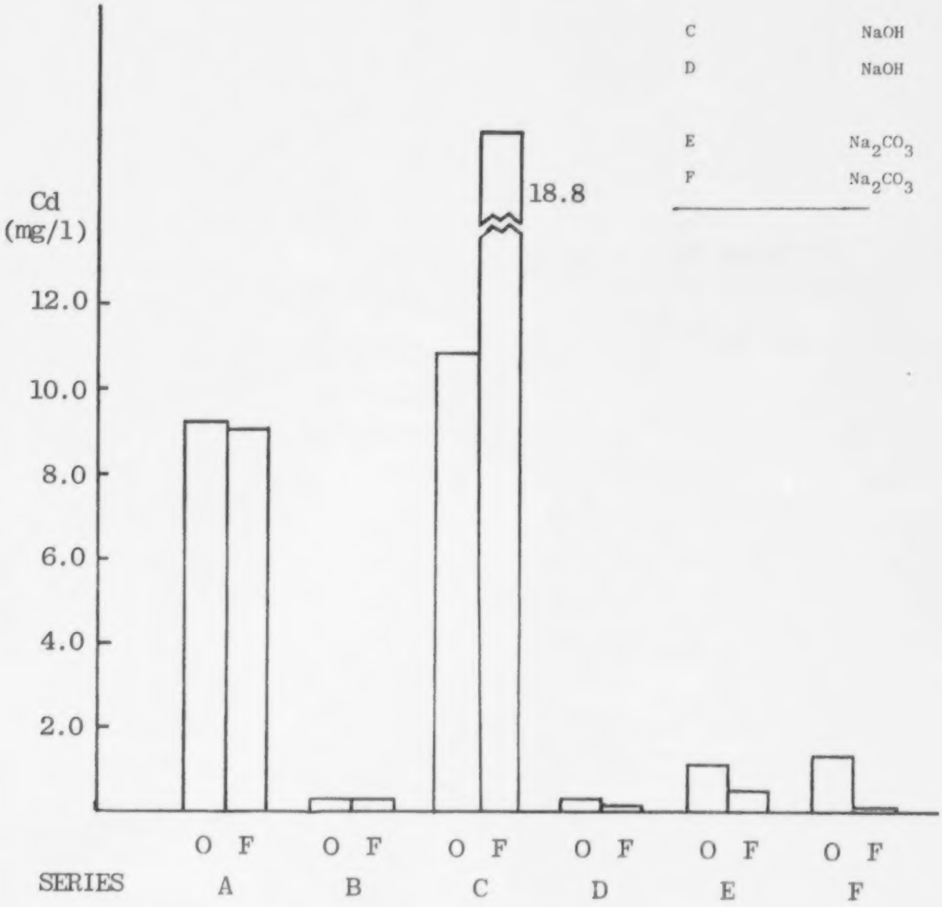
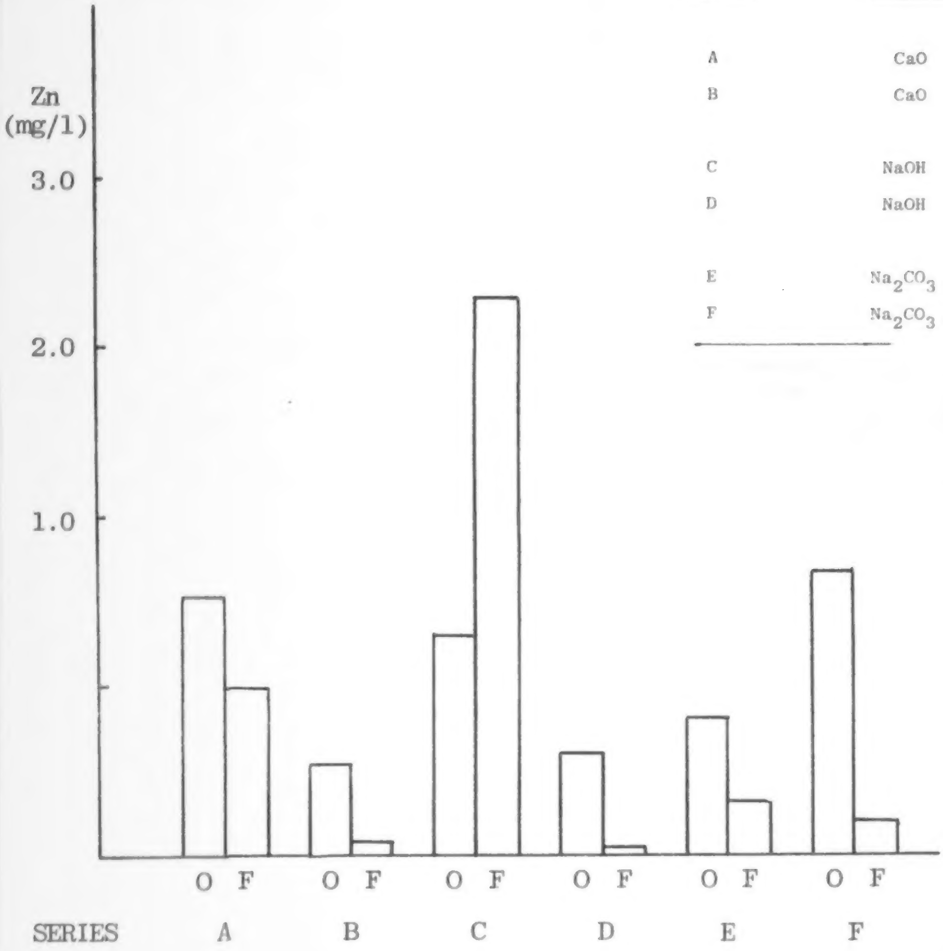


Figure 1. Cadmium levels in the clarifier overflow (O) and the filtrate (F) in the treated wastestream for plant # 2.



SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Figure 2. Zinc levels in the clarifier overflow (O) and the filtrate (F) in the treated wastestream for plant # 2.

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

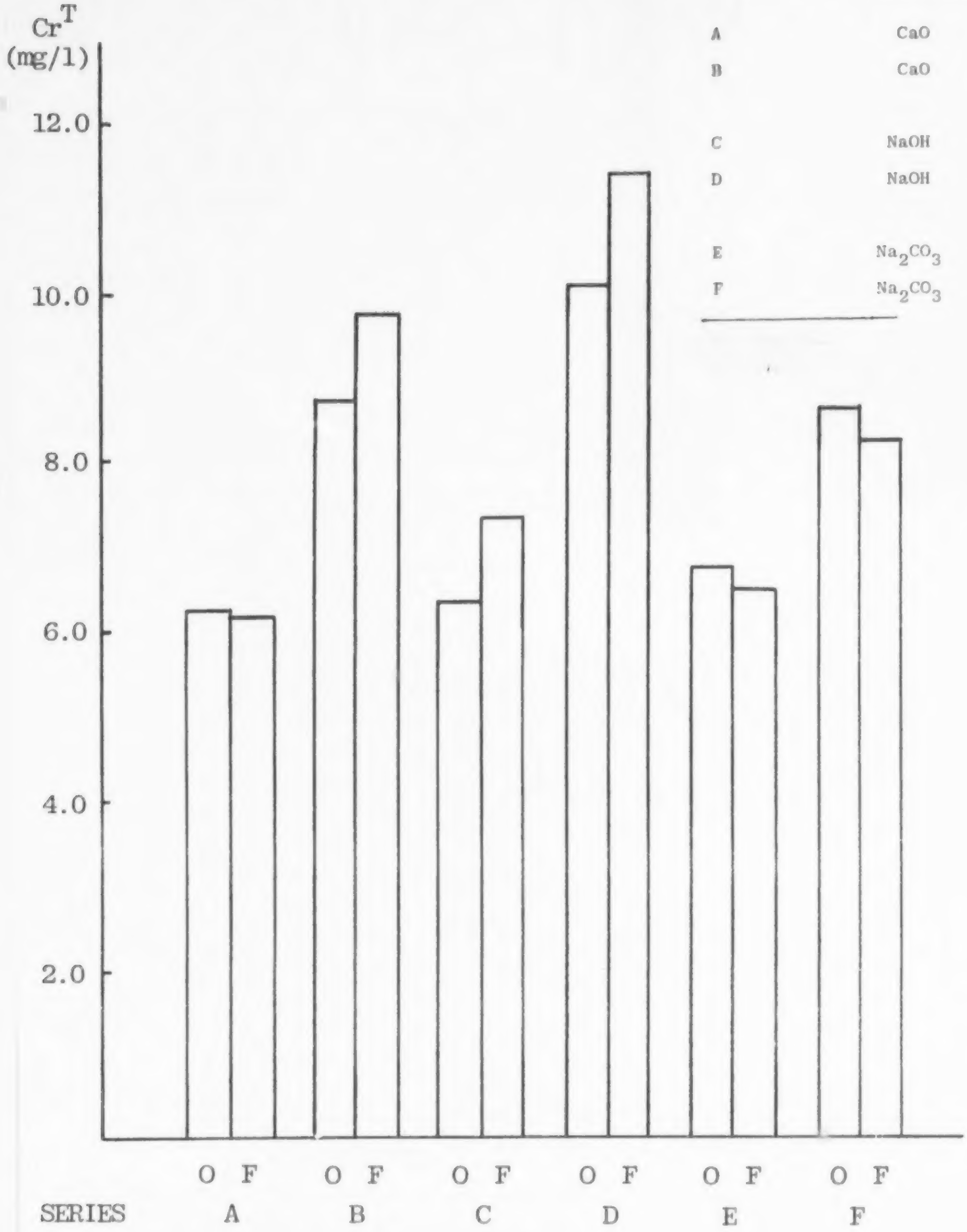


Figure 3. Chromium levels in the clarifier overflow (O) and the filtrate (F) in the treated wastestream for plant # 3.

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

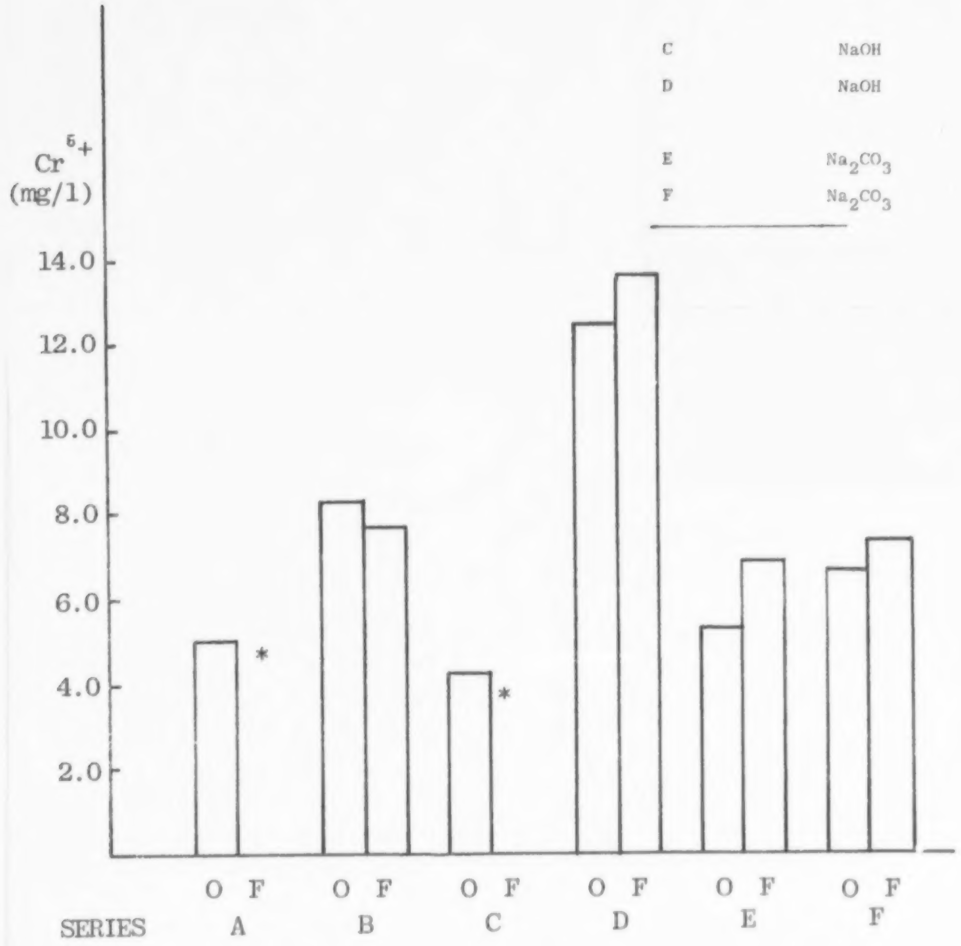


Figure 4. Chromium levels in the clarifier overflow (O) and the filtrate (F) in the treated wastestream for plant # 3.

* Inconsistent data.

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

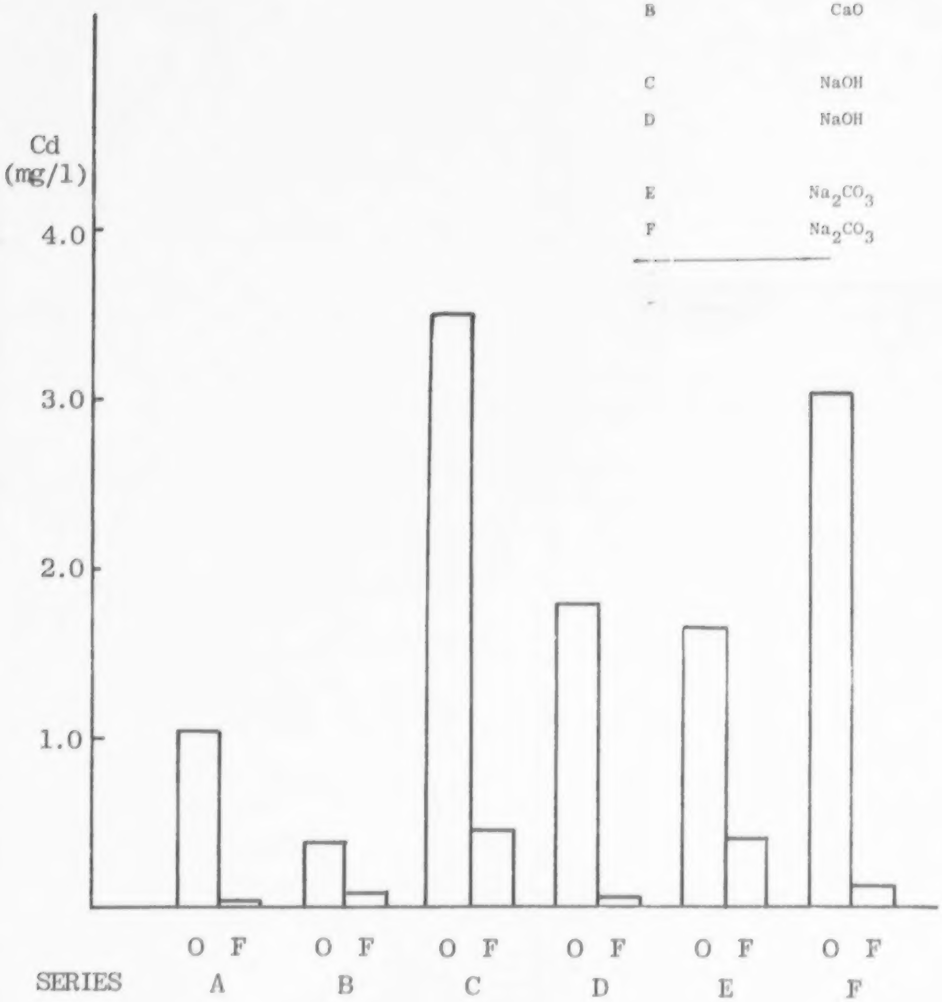


Figure 5. Cadmium levels in the clarifier overflow (O) and the filtrate (F) in the treated wastestream for plant # 3.

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

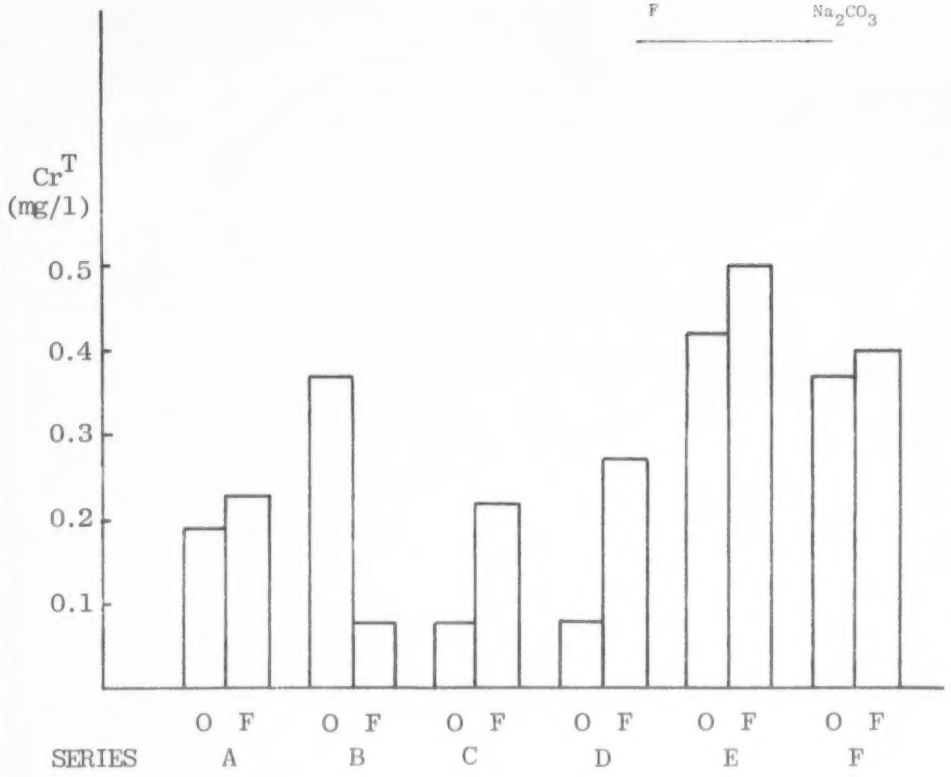


Figure 6. Chromium levels in the clarifier overflow (O) and the filtrate (F) in the treated wastestream for plant # 4.

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

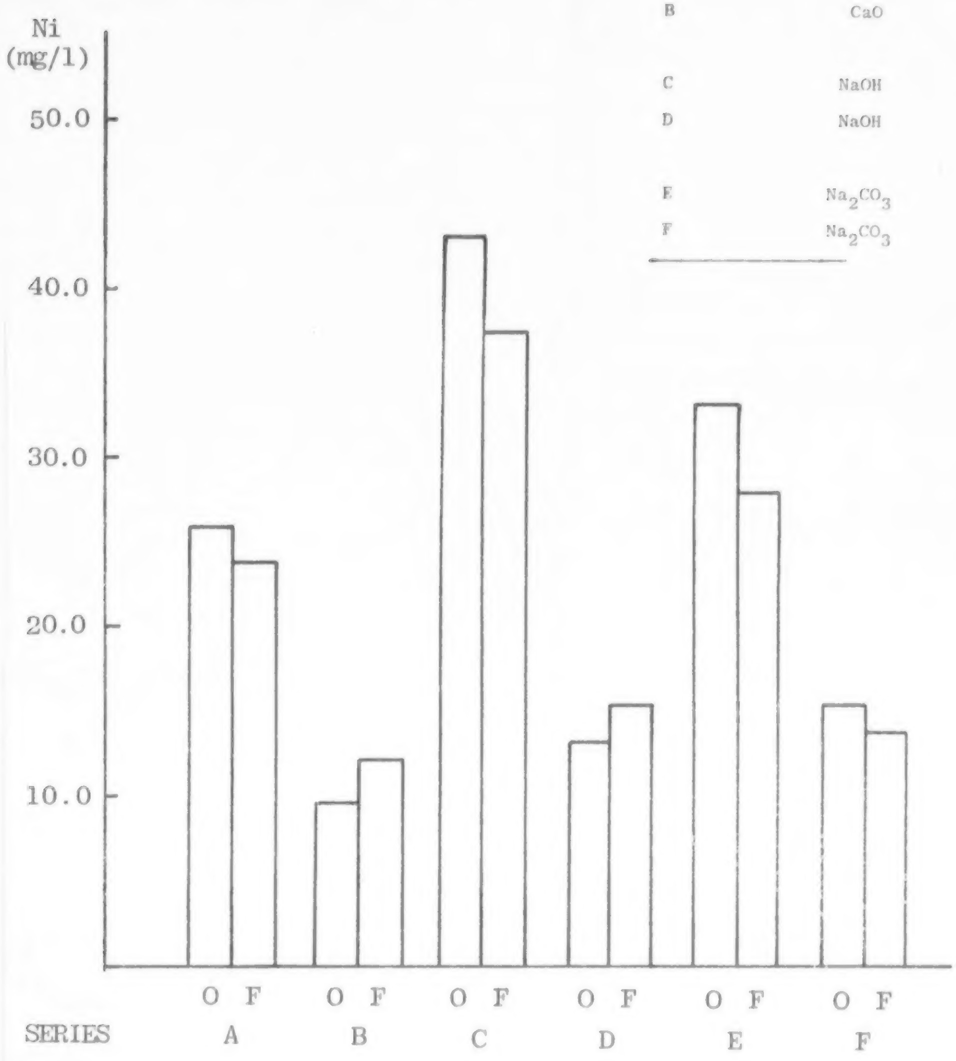


Figure 7. Nickel levels in the clarifier overflow (O) and the filtrate (F) in the treated wastestream for plant # 4.

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

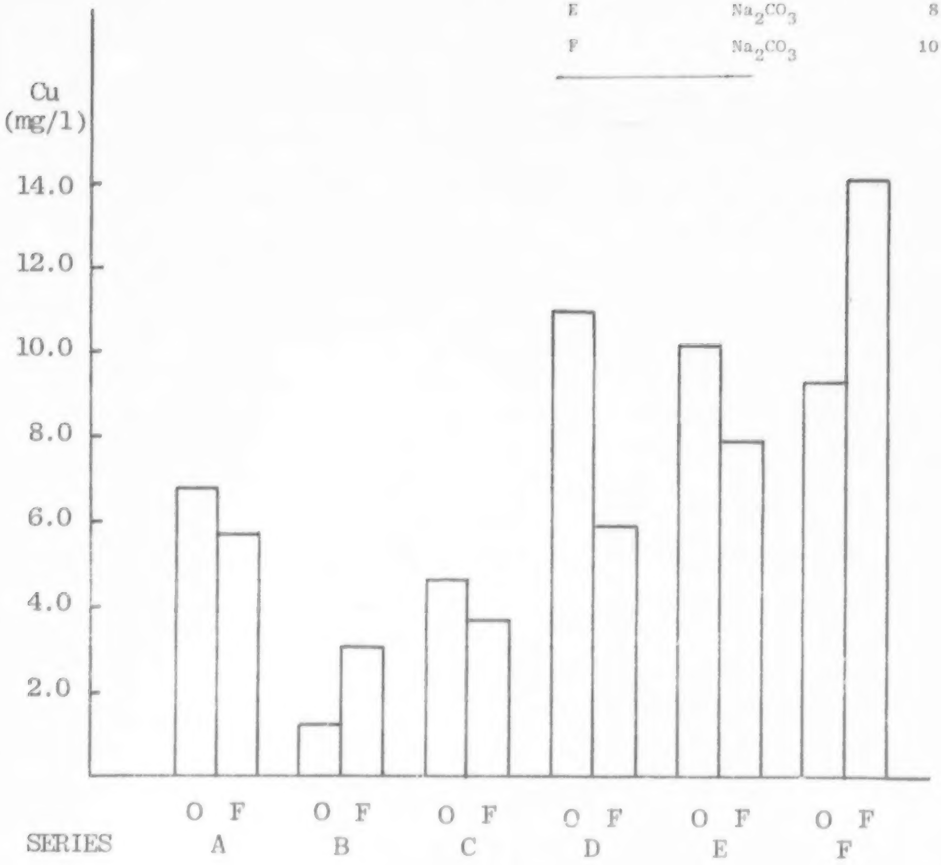


Figure 8. Copper levels in the clarifier overflow (O) and the filtrate (F) in the treated wastestream for plant # 4.

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

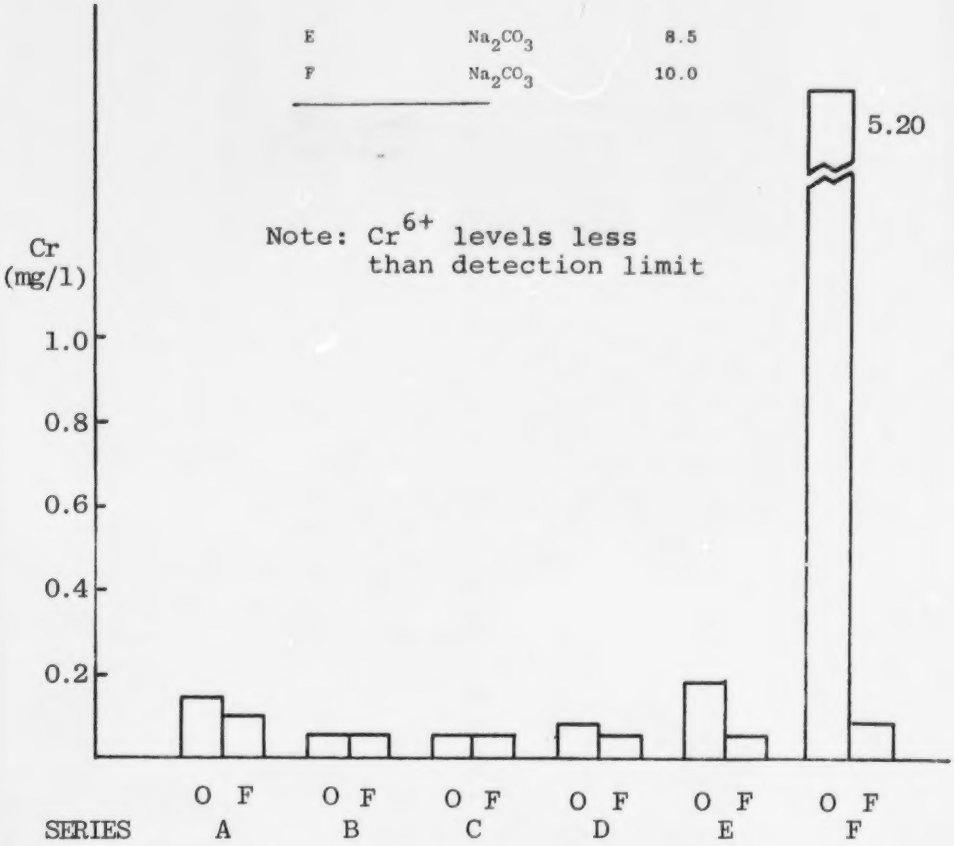


Figure 9. Chromium levels in the clarifier overflow (O) and the filtrate (F) in the treated wastestream for plant # 6.

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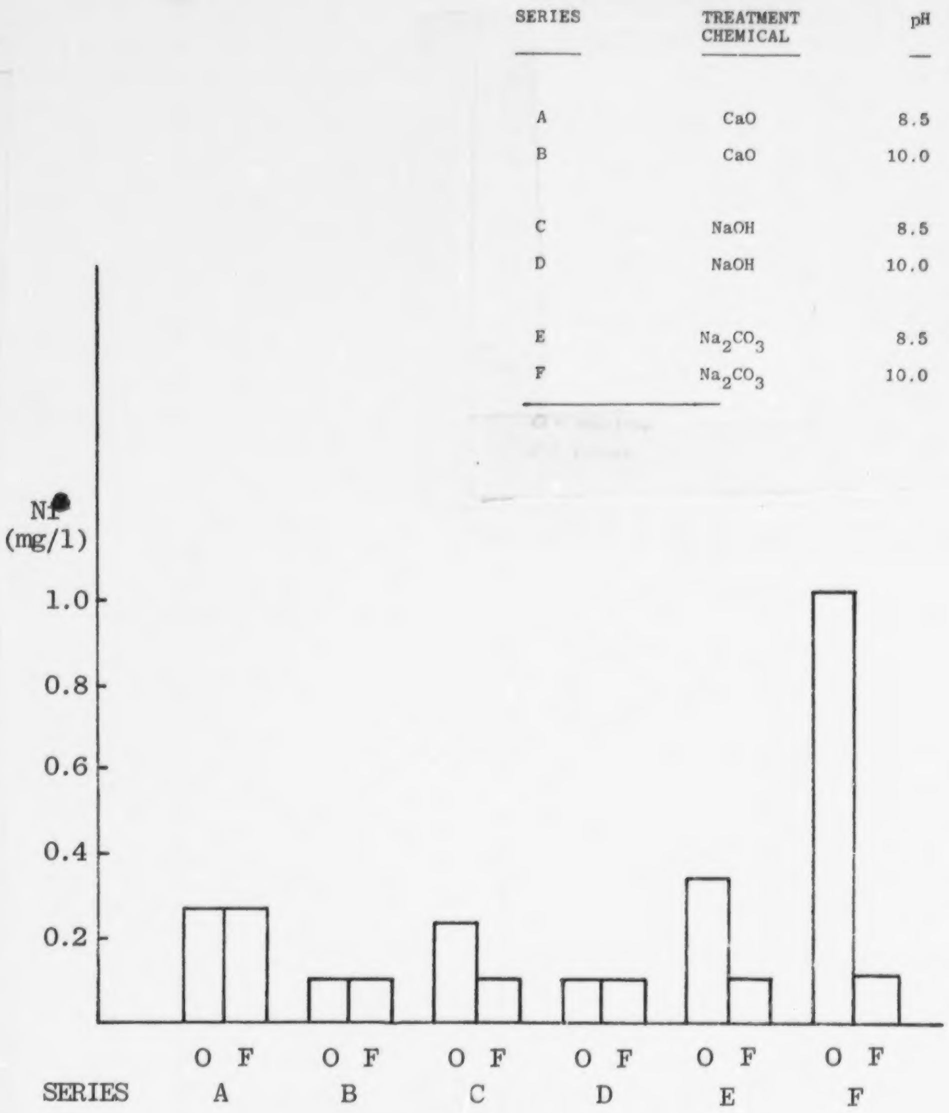

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

Figure 10. Nickel levels in the clarifier overflow (O) and the filtrate (F) in the treated wastestream for plant # 6.

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

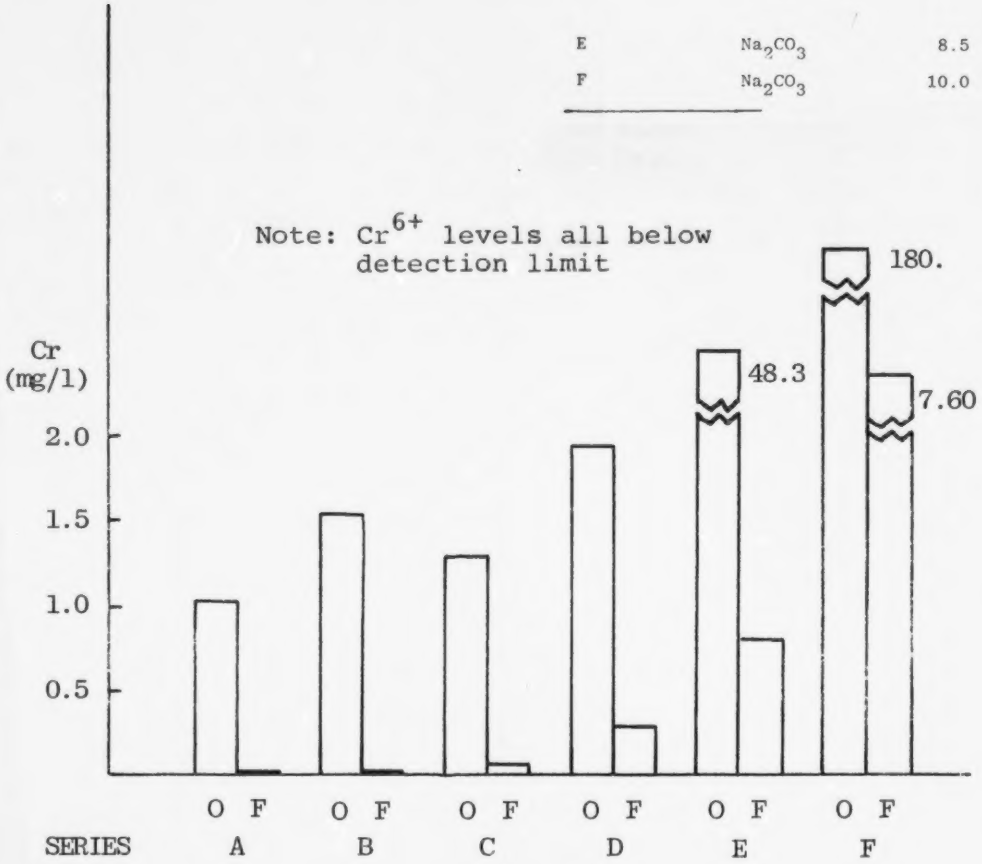
Note: Cr^{6+} levels all below detection limit

Figure 11. Chromium levels in the clarifier overflow (O) and the filtrate (F) in the treated wastestreams for plant # 8.

SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

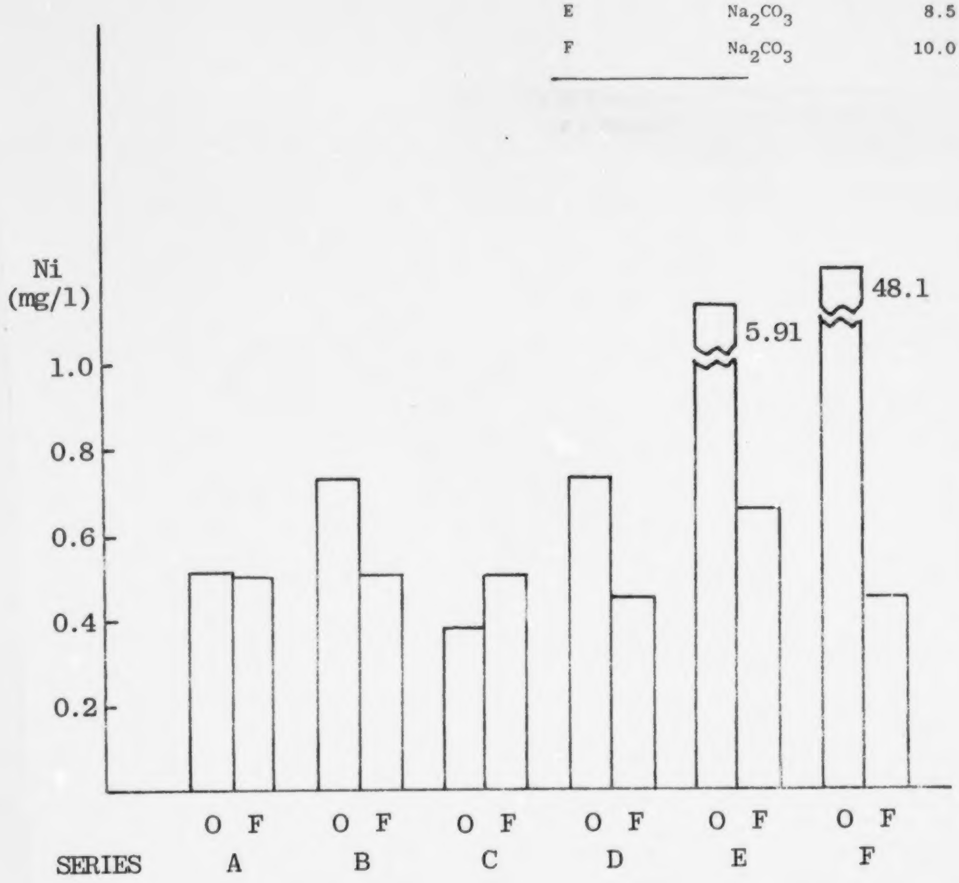

Figure 12. Nickel levels in the clarifier overflow (O) and the filtrate (F) in the treated wastestream for plant # 8.

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SERIES	TREATMENT CHEMICAL	pH
A	CaO	8.5
B	CaO	10.0
C	NaOH	8.5
D	NaOH	10.0
E	Na_2CO_3	8.5
F	Na_2CO_3	10.0

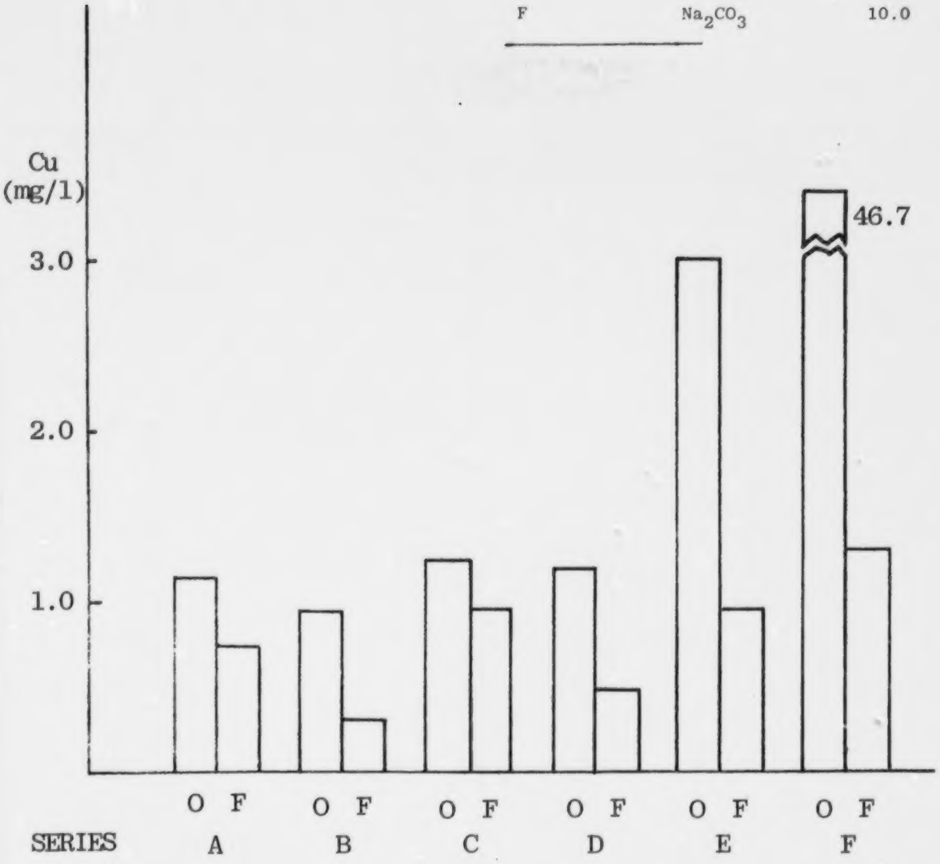

Figure 13. Copper levels in the clarifier overflow (O) and the filtrate (F) in the treated wastestream for plant # 8.

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SECTION 10

CORRELATION OF SCREENING RESULTS FOR PLANTS 2, 3, 4 AND 8

PLANT #2

Correlation Coefficient

	Cr_{tot}	Cr^{+6}	Zn	Cd	Cu	Ni
FILTRATE vs. EP, UNWASHED			.191	.098		
FILTRATE vs. ASTM, UNWASHED			.970	.937		
FILTRATE vs. EP, WASHED			.048	.443		
FILTRATE vs. ASTM, WASHED			.997	.997		
EP, WASHED vs. UNWASHED			.887	.659		
ASTM, WASHED vs. UNWASHED			.995	.998		
WASHED FILTRATE vs. EP, UNWASHED			.397	.343		
EFFLUENT vs. EP, UNWASHED			-.179	-.644		

PLANT #3

Correlation Coefficient

	Cr_{tot}	Cr^{+6}	Zn	Cd	Cu	Ni
FILTRATE vs. EP, UNWASHED	.009	.083		-.234		
FILTRATE vs. ASTM, UNWASHED	.684	.025		.019		
FILTRATE vs. EP, WASHED	.501	.859		.244		
FILTRATE vs. ASTM, WASHED	-.382	-.405		-.244		
EP, WASHED vs. UNWASHED	.706	.585		.961		
ASTM, WASHED vs. UNWASHED	.418	.638		.462		
WASHED FILTRATE vs. EP, UNWASHED	.918	.227		.229		
EFFLUENT vs. EP, UNWASHED	.913	-.172		.341		

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PLANT #4

Correlation Coefficient

	Cr_{tot}	Cr^{+6}	Zn	Cd	Cu	Ni
FILTRATE vs. EP, UNWASHED	-.125	.852			-.048	-.307
FILTRATE vs. ASTM, UNWASHED	.482	.904			.886	.704
FILTRATE vs. EP, WASHED	-.681				-.806	-.852
FILTRATE vs. ASTM, WASHED	.975				.638	.837
EP, WASHED vs. UNWASHED	.447				.683	.815
ASTM, WASHED vs. UNWASHED	-.484				.211	.962
WASHED FILTRATE vs. EP, UNWASHED					-.708	-.772
EFFLUENT vs. EP, UNWASHED	.112	-.030			.483	.322

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PLANT #8

Correlation Coefficient

	Cr_{tot}	Cr^{+6}	Zn	Cd	Cu	Ni
FILTRATE vs. EP, UNWASHED	-.500				-.407	.513
FILTRATE vs. ASTM, UNWASHED	.305				.801	-.373
FILTRATE vs. EP, WASHED	-.576				-.426	.732
FILTRATE vs. ASTM, WASHED	.082				-.277	-.176
EP, WASHED vs. UNWASHED	.924				.746	.918
ASTM, WASHED vs. UNWASHED	-.470				.688	.810
WASHED FILTRATE vs. EP, UNWASHED	-.521				.250	.672
EFFLUENT vs. EP, UNWASHED	-.486				-.214	.497

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SECTION 11

PROPOSED METHODS FOR LEACHING OF WASTE MATERIALS

AMERICAN SOCIETY FOR TESTING AND MATERIALS
1916 Race St., Philadelphia, Pa. 19103
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Proposed Methods for
LEACHING OF WASTE MATERIALS[1]

This proposed method has no status as an ASTM Standard and is published on behalf of the sponsoring committee for information only, for a maximum of two years. Comments are solicited and should be addressed to the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

1. Scope

1.1 These methods cover procedures for leaching of waste materials to obtain an aqueous solution to be used to determine the leachable materials present. The following methods are included:

	Sections
Method A – Water Shake Extraction Procedure	6 to 14
Method B – Acid Shake Extraction Procedure	15 to 23

2. Applicable Documents

2.1 *ASTM Standards:*

D 75 Sampling Aggregates[2]
D 420 Recommended Practice for Investigating and Sampling of Soil and Rock for Engineering Purposes[2]
D 1129 Definitions of Terms Relating to Water[3]
D 1193 Specification for Reagent Water[3]
D 1888 Tests for Particulate and Dissolved Matter in Water[3]
D 2216 Laboratory Determination of Moisture Content of Soils[2]
D 2234 Collection of a Gross Sample of Coal[4]
D 3370 Practices for Sampling Water[3]
E 122 Recommended Practice for Choice of Sample Size to Estimate the Average Quality of a Lot or Process[5]
E 380 Metric Practice[6]

3. Definitions

3.1 For definitions of terms used in these methods, see Definitions D 1129. For an explanation of the metric system including units, symbols, and conversion factors, see Standard E 380.

4. Purity of Reagents

4.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the American Chemical Society, where such specifications are available.[7] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 Unless otherwise indicated, references to water shall be understood to mean Type IV reagent water, Specification D 1193.

5. Sampling

5.1 Obtain a representative sample of the waste to be tested using ASTM sample methods developed for the specific industry where available.

5.2 Where no specific methods are available, sampling methodology for materials of similar physical form should be used.

5.3 A minimum sample of 5000 g shall be sent to the laboratory (see Method E 122).

5.4 Samples should be kept in closed containers appropriate to the sample type prior to testing. Biologically active samples should in the test, report this fact.

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[1] These proposed methods are under the jurisdiction of Committee D-19 on Water.

Published as information only May 1978.

[2] *Annual Book of ASTM Standards*, Part 19.

[3] *Annual Book of ASTM Standards*, Part 31.

[4] *Annual Book of ASTM Standards*, Part 26.

[5] *Annual Book of ASTM Standards*, Parts 15 and 41.

[6] *Annual Book of ASTM Standards*, Part 41 (Excerpts in Part 31).

[7] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N. Y., and the "United States Pharmacopeia."

10.2 For field-cored wastes or castings produced in the laboratory, cut a representative vertical section weighing approximately 350 or 700 g for testing, plus samples for determination of solids content. The sample should be shaped so that the leaching solution will cover the material to be tested.

10.3 For fluid wastes, mix thoroughly in a manner that does not incorporate air to assure uniformity before withdrawing a 350 or 700-g sample for test. Take samples for determination of solids content at the same time as the test sample.

11. Procedure

11.1 Record the physical description of the sample to be tested including particle size so far as it is known.

11.2 *Solids Content* – Determine the solids content of separate portions of the sample as follows:

11.2.1 Dry two dishes or pans of size suitable to the waste being tested at 104 ± 2°C. Cool in a desiccator and weigh. Record the value to ± 0.1 g.

11.2.2 Put an appropriately sized portion of sample of the waste to be tested into each pan. The weight used should be scaled to the physical form of the waste tested. Use a minimum of 50 g but use larger samples where particles larger than 10 mm in average diameter are being tested. Weigh. Record the weight to ± 0.1 g.

11.2.3 Dry 18 ± 2 h at 104 ± 2°C.

11.2.4 Cool to room temperature in a desiccator and reweigh. Record the weight to ± 0.1 g.

11.3 *Shake Procedure* – Weigh or tare the containers to be used in the shake test to 1 g.

11.4 Add to the container approximately 700 g of waste (Sections 7.4 and 10) and determine and record the weight of sample used to 1 g. If weights other than 700 g are used, note in the report.

11.5 Add to the container a volume of test water (9.1) equal in millilitres to four times the weight in grams of the sample used in 11.4.

11.6 Close the container and place it on the agitation equipment.

11.7 Agitate continuously for 48 h ± 0.5 h at 20 ± 2°C.

11.8 Open the containers. Observe and record any changes in the sample and leaching solution.

11.9 Separate the bulk of the aqueous phase from any solid or nonaqueous phases by decantation, centrifugation, or filtration through filter paper as appropriate. Vacuum filter the aqueous phase through a 0.45-μm membrane filter. For oily wastes such as those from API separators, use a 8-μm filter. Retain any nonaqueous liquid separately.

11.10 Transfer the filtrate to sample bottles of a size such that the entire bottle is filled. Close and label. Preserve the filtrate in a manner consistent with the chemical analyses to be performed.

11.11 Analyze the filtrate for specific constituents or properties as desired using appropriate ASTM or other standard methods. Where nonaqueous liquid is present, analyze it also.

12. Calculation

12.1 Calculate the solids content of the individual samples from the data obtained in 11.2 as follows:

$$S = A/B$$

where:

A = weight in grams of sample after drying,
B = original weight in grams of sample, and
S = solid content, g/g.

Average the two values obtained. Record as the solids content.

12.2 Analytical results obtained and reported in milligrams per litre of filtrate may be converted to milligrams leached per gram of dry sample as follows:

$$L = \frac{C}{250\,S}$$

where:

C = concentration of any constituent measured, mg/litre,
S = solids content, g/g and
L = constituent leached in milligrams per gram of dry sample.

13. Report

13.1 The report shall include the following:

13.1.1 Source of the waste and sampling

information,

13.1.2 Description of the waste including physical characteristics and particle size (11.1),

13.1.3 Solids content (11.2),

13.1.4 Sample weight if other than 700 g,

13.1.5 Results of specific analyses calculated in appropriate units (12.2),

13.1.6 Observation of changes in test material or leaching solution recorded in 11.8.

14. Precision

14.1 The precision of analysis for individual constituents is that indicated in their specific methods of analysis.

14.2 The precision of the leaching procedure is to be determined.

METHOD B—ACID SHAKE EXTRACTION PROCEDURE

15. Scope

15.1 This method covers the shaking of a known weight of waste with an acidic buffer solution, and the separation of the aqueous phase for analysis.

16. Significance and Use

16.1 This method is intended as a rapid means of obtaining a solution for evaluation of the extractable materials in waste under acidic conditions. It may be used to produce solutions for the estimation of the relative environmental hazard inherent in the leachings from the waste.

16.2 This method is not intended to produce solutions to be used as a basis for engineering design of disposal sites.

16.3 This method is intended to determine collectively the immediate surface washing and the time-dependent diffusion-controlled contributions to leaching from waste.

16.4 It is intended that the wastes used in this test shall be tested in the physical form in which they will be discarded.

17. Equipment

17.1 Equipment required for this test is described in Section 8.

18. Reagents

18.1 *Sodium Acetate—Acetic Acid Buffer Solution*—Dissolve 4.9 g of glacial acetic acid and 3.7 g of sodium acetate in 1 litre of water. Adjust the pH to 4.5 ± 0.1 by the dropwise addition of acetic acid or sodium hydroxide (40 g/litre) as required. Solution temperature should be 20 ± 2°C.

19. Sampling

19.1 Directions for obtaining a representative sample for test purposes are given in Section 10.

20. Procedure

20.1 Proceed in accordance with Section 11, using the sodium acetate buffer solution (18.1) in place of water in 11.5.

21. Calculation

21.1 Calculate the results obtained as directed in Section 12. The results of specific analyses should be corrected by subtraction of the blank values obtained by analyzing the sodium acetate buffer solution used as the extractant.

22. Report

22.1 Report the results of the test as directed in Section 12.

23. Precision

23.1 No information is presently available as to the precision of the analysis of specific constituents in this test solution. Until this can be done, it is recommended that users of this test check the applicability of their chosen methods of detection by spiking the test water before using these methods for the analysis of the filtrate from wastes.

23.2 The precision of the leaching procedure is to be determined.